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Air Pollution Training Institute
MD 20
Environmental Research Center
Research Triangle Park NC 27711

EPA 450/2-80-004
September 1980

Air

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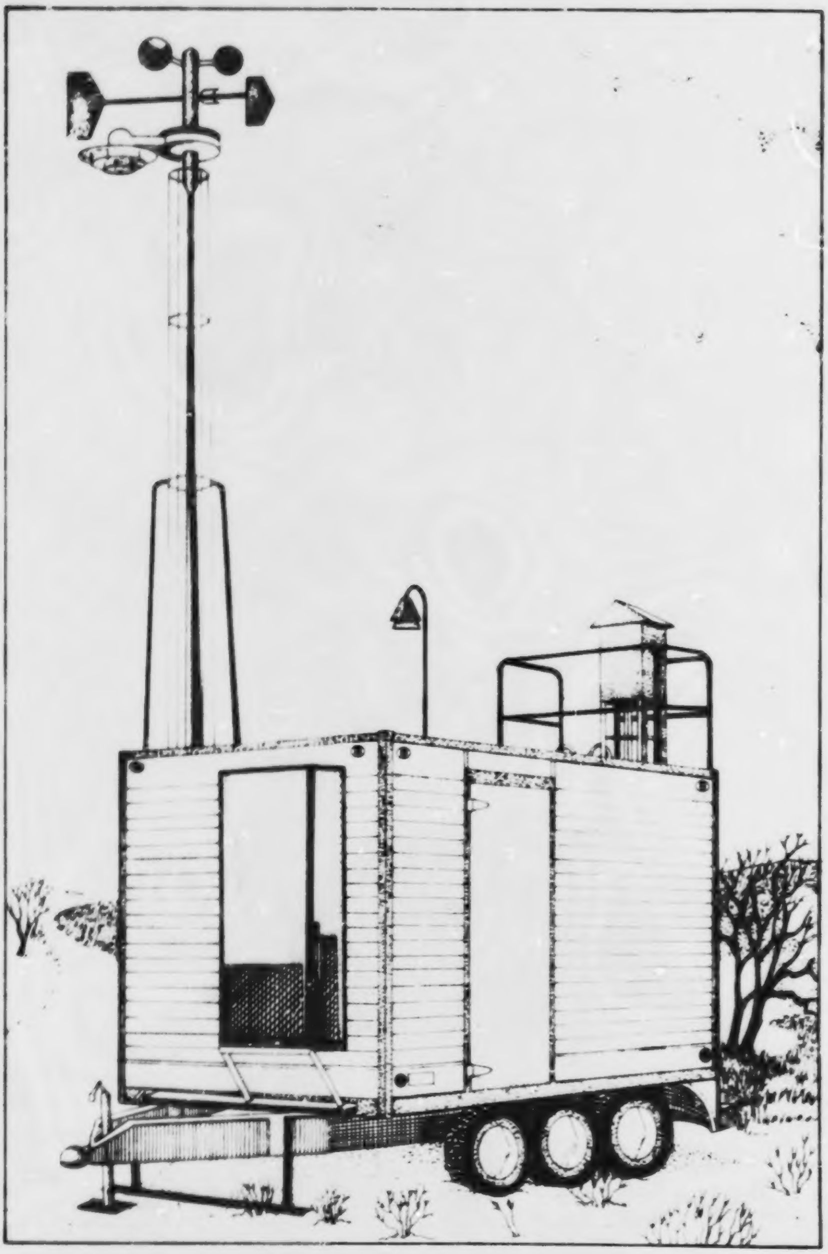
APTI
Course 435
Atmospheric Sampling

COMPLETED

Student Manual



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Course 435
Atmospheric Sampling

Student Manual

Prepared By:
M. L. Wilson
D. F. Elias
R. C. Jordan
O. G. Durham

Revised By:
K.C. Joerger
B.M. Ray

Northrop Services, Inc.
P.O. Box 12313
Research Triangle Park, NC 27709

Under Contract No.
68-02-2374
EPA Project Officer
R.E. Townsend

United States Environmental Protection Agency
Office of Air, Noise, and Radiation
Office of Air Quality Planning and Standards
Research Triangle Park, NC 27711

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MANPOWER AND TECHNICAL INFORMATION BRANCH
CONTROL PROGRAMS DEVELOPMENT DIVISION
OFFICE OF AIR QUALITY PLANNING AND STANDARDS

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R. Alan Schueler

R. Alan Schueler
Program Manager
Northrop Services, Inc.

James A. Jahnke

James A. Jahnke
Technical Director
Northrop Services, Inc.

Jean J Schueneman

Jean J. Schueneman
Chief, Manpower & Technical
Information Branch

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Chapter 1

An Introduction to Atmospheric Sampling

Objectives of Air Monitoring

National Ambient Air Quality Standards (NAAQS) for sulfur dioxide, total suspended particulates (TSP), carbon monoxide, ozone, nitrogen dioxide, nonmethane hydrocarbons, and lead have been established under the authority of the Clean Air Act (as amended August, 1977). There are two types of ambient air quality standards: primary standards and secondary standards. As stated in Section 109 of the Clean Air Act, primary standards are those, "the attainment and maintenance of which are requisite to protect the public health." The section further defines a secondary ambient air quality standard as, "a level of air quality attainment and maintenance of which is requisite to protect the public welfare from any known or anticipated adverse effects associated with the presence of such air pollutants in the ambient air." (1)

These primary and secondary ambient air quality standards must be achieved throughout the United States and its possessions. In order to meet the standards, states are required to develop and implement air pollution control strategies through the mechanism of State Implementation Plans (SIPs). The implementation plans may contain control strategies such as industrial and urban zoning, the development or expansion of mass transit systems and vehicle inspection and maintenance programs, and the establishment of stationary source emissions standards for specific industrial categories. Ambient air monitoring plays a vital role in the development and evaluation of these control strategies. During the development phase, air quality data is used to determine if an area is attaining or not attaining the air quality standards. This determination is critical for the proper designing of control strategies for the area in question because attainment areas usually require less stringent control measures than nonattainment areas. Furthermore, air quality data may be used to generate or validate computer models of air pollution dispersion which are then used in the development of control strategies. After the implementation plans containing their various control strategies have been put into force, further ambient air quality monitoring is required in both attainment and nonattaiment areas. For areas that have achieved attainment, further monitoring is necessary to assure that attainment is maintained. Additional monitoring is required in nonattainment areas for evaluating progress towards reaching attainment. (2)

In addition to the requirement that the primary and secondary National Ambient Air Quality Standards be achieved and maintained throughout the country, the Clean Air Act also stipulates that no significant deterioration of existing air quality will be allowed in any portion of any state. In order to comply with this provision, it is necessary to determine the impact on the already existing air quality of an area by a planned new emissions source. The estimated emissions contributed by the new source must be compared to the already existing air quality to ascertain whether the new source would significantly deteriorate the present air quality. Ambient air quality monitoring data is used to establish the preexisting air quality of the area in question.

It should be recognized that the overall goal of an air quality monitoring network is the protection of human health and welfare. The aforementioned monitoring objectives should assure the attainment of this goal under ordinary circumstances. However, abnormal meteorological conditions, such as temperature inversions, which cause poor air pollutant dispersion may result in the formation of pollutant levels that could cause significant harm to public health. These significant harm levels are listed in Figure 1-1. Air pollution emergency episode plans are utilized to prevent pollutant levels from reaching concentrations which would cause significant harm to the health of persons. The plans specify incremental reductions of source emissions based on up-to-date ambient air monitoring data.(3)

Pollutant	**Concentration**	**Units**	**Averaging time**
SO_2	2620 1.0	$\mu g/m^3$ ppm	24 hr.
Particulate matter (TSP)	1000	$\mu g/m^3$	24 hr.
SO_2x particulate	490×10^3	$(\mu g/m^3)^2$	24 hr.
CO	57.5 50	mg/m^3 ppm	8 hr.
	86.3 75	mg/m^3 ppm	4 hr.
	144 125	mg/m^3 ppm	1 hr.
Ozone	1200 0.6	$\mu g/m^3$ ppm	1 hr.
NO_2	3750 2.0	$\mu g/m^3$ ppm	1 hr.
	938 0.5	$\mu g/m^3$ ppm	24 hr.

Figure 1-1. Significant harm levels established by the Environmental Protection Agency.

Sampling Train Design

Most atmospheric sampling techniques make use of a sampling train similar to the block diagram in Figure 1-2. Air containing the pollutant of interest enters the sampling train and passes through a sample collection device. This device either physically or chemically removes the pollutant from the air stream, holds the polluted air for later analysis, or allows the pollutant to be analyzed simultaneously with the collection. Ideally, only the pollutant of interest is collected. This is seldom the case, however; hence, interferences must be considered when measurements are made.

Many sampling techniques use collection devices that remove the pollutant from the air for later analysis. Wet chemical methods, such as the pararosaniline method for sulfur dioxide (SO_2), remove the pollutant from the air and hold the pollutant by means of a chemical reaction for later analysis. In the pararosaniline method, the sample collection device is a bubbler containing an absorbing reagent. The High Volume method for total suspended particulates (TSP) uses a filter as the sample collection device. In either case, the pollutant is held by the collector for analysis by a contaminant detector. The contaminant detector in the pararosaniline method is analysis by colorimetry; for TSP High Volume sampling, it is a gravimetric balance.

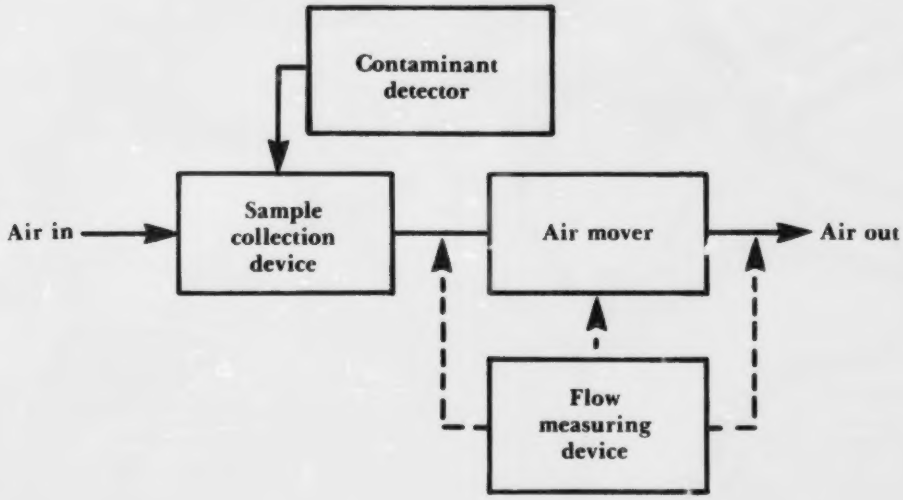

Figure 1-2. Typical sampling train.

Instrumental methods such as chemiluminescence for nitrogen dioxide (NO_2) and ozone (O_3) combine the sample collector and the contaminant detector into one device.

Some methods of air sampling are used that collect a volume of polluted air for later analysis. These methods usually make use of grab or integrated sampling using containers made of stainless steel, glass, pliable plastic or simple hypodermic syringes. Many factors are important in considering what material should be used when grab sampling (4); many uses have been found for plastic bags. In this type of sampling, the plastic bag, syringe, stainless steel or glass container, is the sample collection device. Contaminant detection is usually by instrumental analysis.

Mechanisms used to move air through the sample collection device and measure the quantity of air are integral parts of sampling trains. Air movers are usually motor driven pumps. When motor driven pumps are not practical, ejectors, displacement methods, and evacuated flasks can be used. Some typical flow measuring (or controlling) devices for sampling are: rotameters, mass flow meters, and critical and subcritical orifices. It is often necessary to determine how long an air mover has pulled a certain flow rate to determine the volume sampled (*volume = flow rate × time*); therefore, the time sampled is data that is recorded. Placement of the flow measuring device is dependent on what device is used. Air movers and flow measuring devices are usually placed after sample collection devices to avoid contamination of the air stream.

Materials used in a sampling train (at least to as far as the collector) must be sufficiently inert to the pollutant of interest so as not to interfere with collection. If the air mover and flow measuring device must be placed before the collection step, then parts of those devices contacting the air stream must be inert. Glass, Teflon®, and stainless steel are generally considered to be nonreactive. Hence, these materials have been used extensively in sampling train construction. However, the materials listed as being generally nonreactive can become reactive if used to sample the wrong environment. For instance, glass could not be used if a sampling train was being built to monitor hydrofluoric acid. Even if a material is considered nonreactive, significant wall loss can occur if sampling lines are too long.

Interference with the measurement of an air pollutant is not the only consideration important to the selection of sampling train materials. Care must be taken to protect sampling train components from damage caused by the sampled air or products of the measurement system. If a rubber diaphragm pump is to be used in conjunction with an analyzer that measures nitrogen oxides by the reaction of nitric oxide (NO) with ozone (O_3), then a charcoal filter must be used before the pump to remove excess ozone. If ozone is allowed to contact the rubber diaphragm of the pump, the rubber will deteriorate. Other sampling train components that usually need protection are rotameters and small orifice meters. In this case, a filter and moisture trap are placed in front of the orifice or rotameter to prevent them from becoming clogged.

References

Note: Some references may not be referred to in the text. They are supplied for additional reference.

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2. *Air Monitoring Strategy for State Implementation Plans.* EPA-450/2-77-010. June 1977.
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Chapter 2

Basic Gas Properties and Mathematical Manipulations

Temperature

The Fahrenheit and Celsius Scales

The range of units on the Fahrenheit scale between the freezing and boiling point of water at one atmosphere (atm) pressure is 180 (212°F − 32°F = 180°F); on the Celsius or Centigrade scale, the range is 100 (100°C − 0°C = 100°C). Therefore, each Celsius degree is equal to 9/5 or 1.8 Fahrenheit degrees. To be able to convert from one system to the other, the following equations can be used:

(Eq. 2-1) $$°F = 1.8°C + 32$$

(Eq. 2-2) $$°C = \frac{(°F - 32)}{1.8}$$

Where: °F = degrees Fahrenheit
°C = degrees Celsius or degrees Centigrade

Absolute Temperature

Experiments in which a gas volume is determined as a function of temperature (at a constant pressure) yield results similar to the data presented in Figure 2-1(a). The solid portion of each line represents the gaseous state. If each line is extrapolated (dashed portion of line) to a volume of zero, they all intersect at a common temperature (−273.15°C or −459.67°F). This is the temperature at which a gas, if it did not condense, would theoretically have a volume of zero. This temperature (−273.15°C or −459.67°F) is called ***absolute zero***. Another temperature scale, developed by and named after English physicist Lord Kelvin, begins at absolute zero and has temperature intervals equal to Centigrade units. This absolute temperature scale is in units of ***degrees Kelvin*** (°K). A similar scale was developed to parallel the Fahrenheit scale and is called the ***Rankine scale*** (°R). The following formulas can be used to convert temperatures to their respective absolute scale.

(Eq. 2-3) $$°K = °C + 273.16$$

(Eq. 2-4) $$°R = °F + 459.67$$

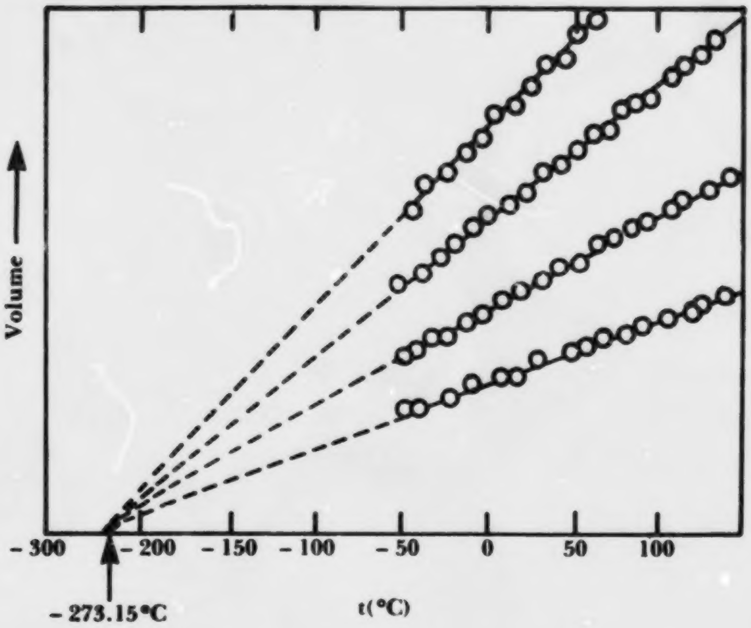


Figure 2-1(a). Temperature relationships.

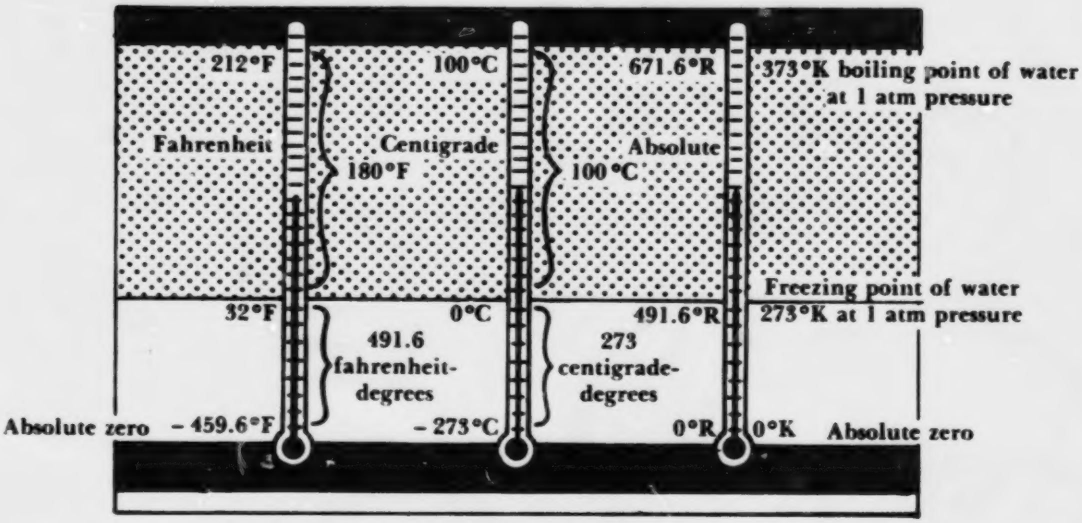

212°F
100°C
671.6°R
373°K boiling point of water at 1 atm pressure
Fahrenheit
Centigrade
Absolute
180°F
100°C
Freezing point of water
32°F
0°C
491.6°R
273°K at 1 atm pressure
491.6 fahrenheit-degrees
273 centigrade-degrees
Absolute zero
- 459.6°F
- 273°C
0°R
0°K
Absolute zero

Figure 2-1(b). Relationships of the absolute temperature systems.

Relationship of the absolute temperature systems are shown graphically in Figure 2-1(b). The symbol "T" will be used throughout this manual to denote absolute temperatures and the "t" will be used to indicate Fahrenheit or Centigrade degrees. The absolute temperatures are always in volume calculations involving temperature and pressure.

Pressure

Definition of Pressure

A body may be subject to three kinds of stress: shear, compression, and tension. Fluids are unable to withstand tensile stress; hence, they are subject to shear and compression only. *Unit compressive stress in a fluid is termed pressure* and is expressed as *force per unit area*.

Pressure

Metric	English
gm_f/cm^2	lb_f/in^2 (psi)

Pressure is equal in all directions at a point within a volume of fluid and acts perpendicular to a surface.

Barometric Pressure

Barometric pressure and atmospheric pressure are synonymous. These pressures are measured with a barometer and are usually expressed as inches, or millimeters, of mercury. *Standard barometric pressure is the average atmospheric pressure at sea level, 45° north latitude at 35°F and is equivalent to a pressure of 14.696 pounds-force per square inch exerted at the base of a column of mercury 29.921 inches high (in the English System). In the metric system, standard barometric pressure is equivalent to a pressure of 1033.23 grams-force per square centimeter exerted at the base of a column of mercury 760 mm high*. Weather and altitude are responsible for barometric pressure variations.

Torricelli Barometer

The Torricelli or mercurial barometer was first used by one of Galileo's students, Torricelli, in 1643. A mercurial barometer is made by sealing a tube, about 32 inches long, at one end. The tube is filled with mercury. It is then inverted and placed into a container that is partially filled with mercury. The mercury in the tube will fall until the weight of the mercury in the tube is equal to the force of the air pressure on the mercury in the container. As shown in Figure 2-2, the manometer and the mercurial barometer work on the same principle—atmospheric pressure being measured with reference to a vacuum.

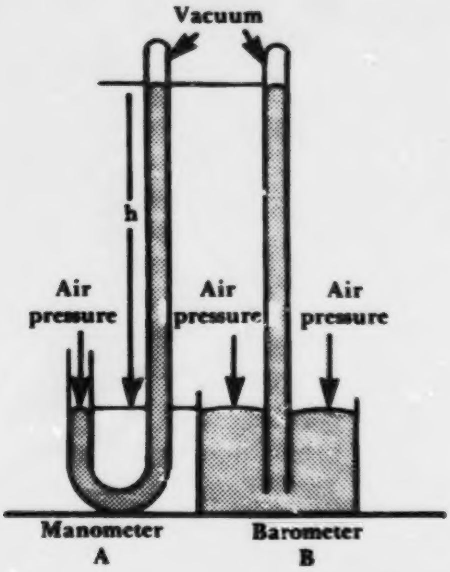

Vacuum
h
Air pressure
Air pressure
Air pressure
Manometer A
Barometer B

Figure 2-2. The manometer and mercurial barometer.

Fortin Barometer

Since the mercurial barometer is the most accurate measurement (calibration uncertainty of 0.001 to 0.03% of reading) of atmospheric pressure, it is still in wide use today. The most common modified version of the mercurial barometer is the Fortin type shown in Figure 2-3

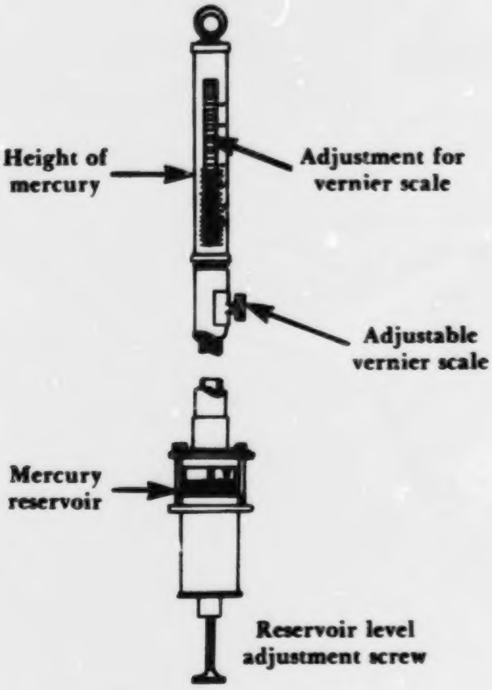

Height of mercury
Adjustment for vernier scale
Adjustable vernier scale
Mercury reservoir
Reservoir level adjustment screw

Figure 2-3. Fortin barometer.

The height of the mercury column in a Fortin barometer is measured from the tip of the ivory index point (see the enlargement in Figure 2-4) to the top of the mercury column. The mercury level in the glass cylinder (ambient-vented cistern) is adjusted until the ivory index point just pricks the surface of the mercury. This is done by turning the datum-adjusting screw. Then the vernier scale is adjusted until the bottom of it is even with the top of the mercury meniscus. After the vernier scale is adjusted, the height of the mercury column is read.

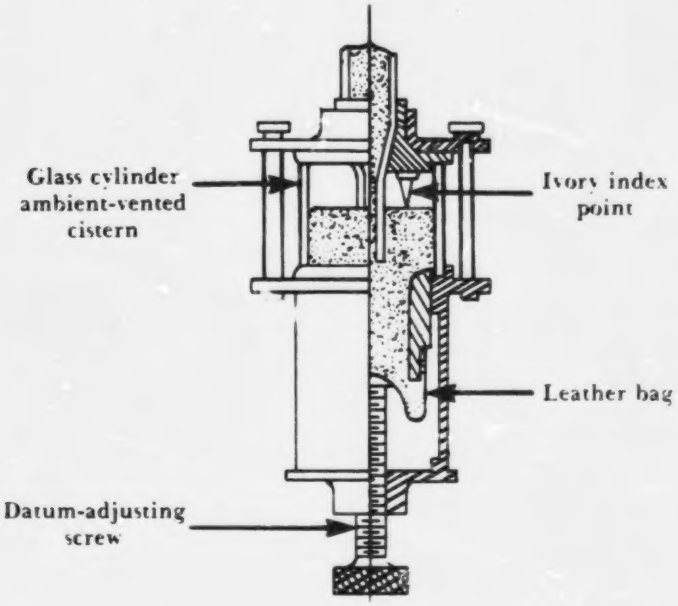

Glass cylinder ambient-vented cistern
Ivory index point
Leather bag
Datum-adjusting screw

Figure 2-4. Blow-up of Fortin barometer.

A typical vernier scale is shown in Figure 2-5. The barometric pressure indicated in the figure is determined in the following way:

> The bottom of the vernier scale indicates not only the integer component of the barometric pressure, but also the tenths components, in this case, 29.9. The hundredths component is indicated by the match between the outer scale and the vernier, in this case, 0.04. The readings are totaled to determine the barometric pressure: 29.9 + 0.04 = 29.94 in Hg. The equivalent metric reading is 76.05 cm.

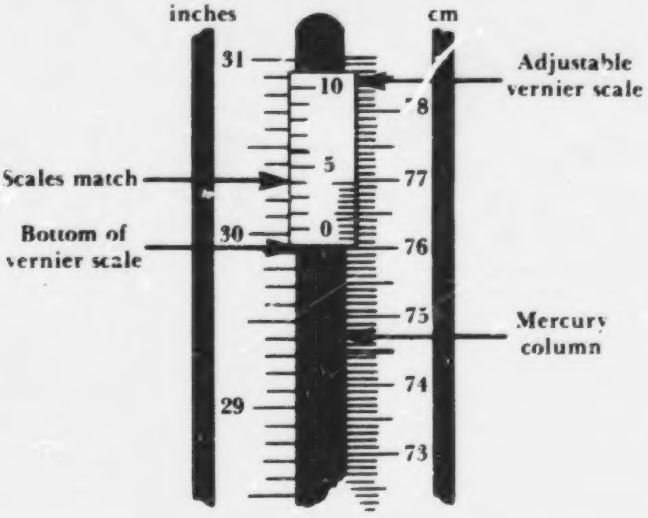


Figure 2-5. Blow-up of Vernier scale

Aneroid Barometer

The aneroid barometer is usually not as accurate as a Torricelli barometer. However, aneroid barometers are more widely used because they are smaller, more portable, less expensive, and easier to adapt to recording instrumentation than are Torricelli barometers.

The aneroid barometer usually consists of a metal chamber, bellows, or sylphon cell (accordian-like) that is partially evacuated. A spring is used to keep the metal chamber from collapsing (see Figure 2-6). The width of the chamber is determined by the balance between the spring and the force exerted by the atmosphere. The width of the chamber is indicated by a pointer and scale that can be calibrated to read directly in units of pressure (i.e., millimeters or inches of mercury, etc.). The pointer movement can be amplified by using levers. Read-out systems can vary from visual scales to recording devices. The combination of an aneroid barometer and an automatic recording device is called a barograph.

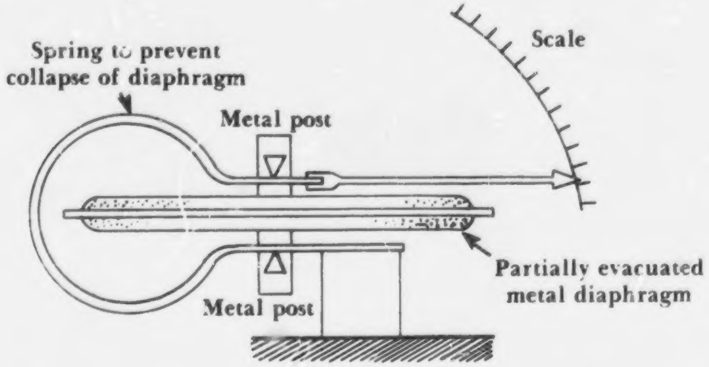

Spring to prevent collapse of diaphragm
Scale
Metal post
Partially evacuated metal diaphragm
Metal post

Figure 2-6. Aneroid barometer.

Pressure Transducers

A transducer is a device that is activated by power from one system and supplies power in some other form to a second system. Conventional pressure transducers use an elastic element that converts the energy from a pressure differential into a displacement of a mechanical device. An example of a mechanical pressure transducer is shown in Figure 2-7. Other pressure transducers convert the mechanical displacement into an electrical signal. An example of an electrical transducer is shown in Figure 2-8. Electrical pressure transducers have become very popular because the signal is easy to measure, control, amplify, transmit, and record.

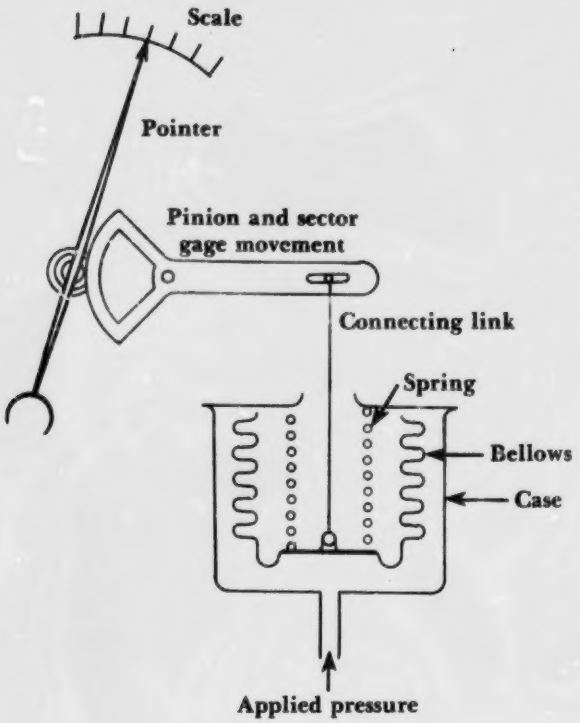

Scale
Pointer
Pinion and sector gage movement
Connecting link
Spring
Bellows
Case
Applied pressure

Figure 2-7. Mechanical pressure transducer.

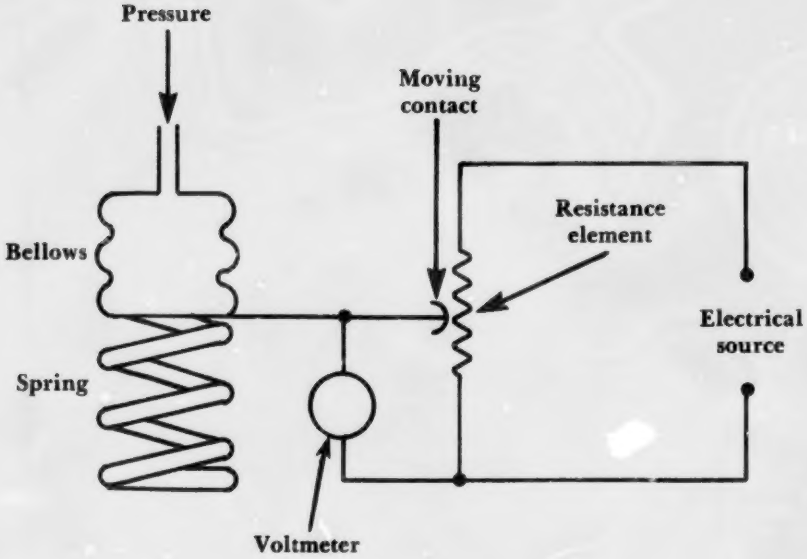

Pressure
Moving contact
Resistance element
Bellows
Electrical source
Spring
Voltmeter

Figure 2-8. Electrical pressure transducer.

Gage Pressure

Gages indicate the pressure of the system of which they are a part relative to ambient barometric pressure. If the pressure of the system is greater than the pressure prevailing in the atmosphere, the gage pressure is expressed as a positive value; if smaller, the gage pressure is expressed as a negative. The term "vacuum" designates a negative gage pressure.

The abbrevation "*g*" is used to specify a gage pressure. For example, *psig*, means pounds-force per square inch gage pressure.

Absolute Pressure

Because gage pressure (which may be either positive or negative) is the pressure relative to the prevailing atmospheric pressure, the gage pressure, added algebraically to the prevailing atmospheric pressure (which is always positive), provides a value that is called "absolute pressure." The mathematical expression is:

(Eq. 2-3)

$$P = P_b + p_g$$

Where:

P = absolute pressure

P_b = atmospheric pressure

p_g = gage pressure

Note: P, P_b, and p_g must be in the same units of pressure before they can be added (i.e., all must be in inches of mercury, mm of mercury, etc.).

The abbrevation "*a*" is sometimes used to indicate that the pressure is absolute. For example, *psia*, means pounds per square inch absolute pressure.

Equation 2-3 allows conversion of one pressure system to the other. Relationship of the pressure system is shown graphically in Figure 2-9 using two typical gage readings, 1 and 2. Gage reading 1 is above the prevailing atmospheric pressure, and, hence, is expressed as a positive value. Gage reading 2 is below the prevailing atmospheric pressure and, therefore, is expressed as a negative value. Gage reading 3 has both sides open to the atmosphere, hence, the gage pressure is zero.

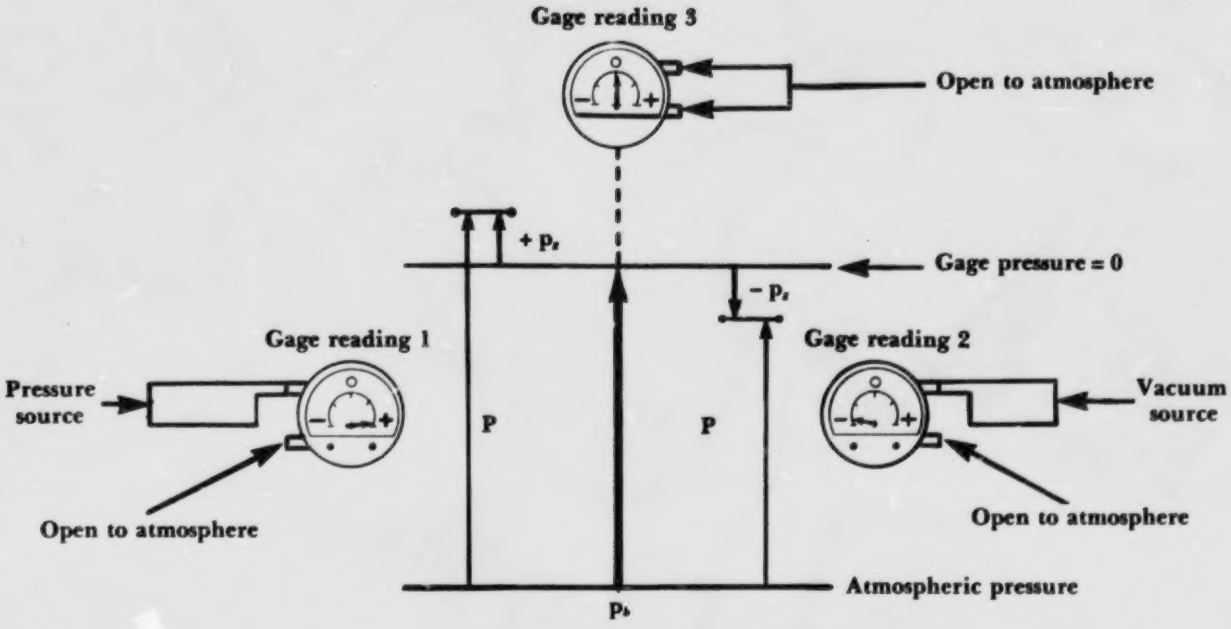

Gage reading 3
Open to atmosphere
+ p_g
Gage pressure = 0
− p_g
Gage reading 1
Gage reading 2
Pressure source
Vacuum source
P
P
Open to atmosphere
Open to atmosphere
Atmospheric pressure
P_b

Figure 2-9. Absolute-atmospheric-gage pressure relationship.

Example Problems

Problem 1:
The primary *pressure* gage of a regulator attached to a compressed nitrogen cylinder indicates a reading of 2000 *psig*. An aneroid barometer mounted on the wall indicates that the atmospheric pressure is 14.2 *psi*. What is the absolute pressure inside the tank?

Solution: $P = P_b + p_g = 14.2 + 2000$
$P = 2014.2$ *psia*

Problem 2:
A water manometer is used to measure the pressure inside an evacuated flask. The water manometer indicates that the evacuated flask has a vacuum of 26 inches of water. A nearby Fortin barometer indicates that atmospheric pressure is 752.6 mm Hg. What is the absolute pressure inside the flask?

Solution:
Before p_g and P_b can be added to give P, both must be in the same unit of pressure. It is most common for p_g to be converted to the same units as P_b since P_b is in much larger units.

Since 1 inch of Hg = 13 inchs H_2O (Hg is 13 times denser than water)

$$\left(26 \text{ inches } H_2O\right)\left(\frac{1 \text{ inch Hg}}{13 \text{ inches } H_2O}\right)\left(\frac{25.4 \text{ mm}}{1 \text{ inch}}\right) = 50.8 \text{ mm Hg}$$

Now p_g and P_b can be added. p_g is negative because the evacuated flask is at a *vacuum or below atmospheric pressure.*

$$P = P_b + p_g = 752.6 \text{ mm Hg} + (-50.8 \text{ mm Hg})$$
$$P = 701.8 \text{ mm Hg}$$

The Concept of Pressure-Head

Pressure-head is the height of a column of fluid required to produce a given pressure at its base.

The relationship between pressure and pressure-head is:

(Eq. 2-4) $$p = \varrho_f h\left(\frac{g}{g_c}\right)$$

Where:
p = *pressure, force/area*
ϱ_f = *density of fluid, mass/volume*
g = *local acceleration due to gravity, length/time*^{2}
g_c = *dimensional constant*
h = *pressure-head in terms of* ϱ_f, *length*

Pressure-head may be expressed in terms of any fluid that is convenient: e.g., Hg or H_2O.

Dalton's Law of Partial Pressure

When gases or vapors (having no chemical interaction) are present as a mixture in a given space, the pressure exerted by a component of the gas-mixture at a given temperature is the same as it would exert if it filled the whole space alone *The pressure exerted by one component of a gas-mixture is called its partial pressure. The total pressure of the gas-mixture is the sum of the partial pressures.*

Expressed mathematically:

$$P_{total} = \Sigma p_i$$

Where:
P_{total} = *total pressure exerted by the system*
p_i = *pressure of each component of the system*
$\Sigma p_i = p_1 + p_2 + \ldots + p_n$
(Σ: means "sum of")

The Ideal Gas Laws

Ideal gases are gases whose molecules do not attract one another and which occupy no part of the whole volume. Although there are no gases which have these properties, real gases, which deviate very slightly from ideal gas behavior under ordinary temperature and pressure conditions, may be considered to be ideal gases.

Boyle's Law

Boyle's Law states: when the *temperature* (T) is held constant, the *volume* (V) of a given mass of an ideal gas of a given composition varies inversely as the absolute pressure, i.e.:

$$V \alpha \frac{1}{P} \text{(at constant } T\text{)}$$

Where: α = *proportional to.*

One can see that, as the pressure on a gas system increases, the volume of the gas system will decrease and vice versa.

Charles' Law

Charles' Law states: when the *pressure* (P) is held constant, the *volume* (V) of a given mass of an ideal gas of a given composition varies directly as the *absolute temperature* (T), i.e.,:

$$V \alpha T \text{ (at constant } P\text{).}$$

In other words, as the temperature of a gas system increases, the volume will also increase and vice versa.

The Law for Ideal Gases

Both Boyle's and Charles' Law are satisfied in the following equation:

$$PV = nRT \tag{Eq. 2-5}$$

Where:
P = *absolute pressure*
V = *volume of a gas*
T = *absolute temperature*
R = *universal gas-constant*
n = *number of moles of a gas.*

A *mole* of a substance is the substance's molecular weight expressed in mass units. Where the substance's molecular weight is the sum of the atomic weights of the atoms which compose the substance.

We know that

$$n = \frac{m}{M}$$

Where: m = *mass of a gas*
M = *molecular weight of a gas*

therefore:

$$PV = nRT = \frac{m}{M} RT$$

The units of R depend upon the units of measurement used in the equation. Some useful values are:

(1) $R = 0.082\ (\ell)\ (atm)\ (°K)^{-1}(g\text{-}mole)^{-1}$
(2) $R = 62.4(\ell)(mm\ Hg)(°K)^{-1}(g\text{-}mole)^{-1}$

Where the units are: V (ℓ)
m (g)
M (g/g-*mole*)
T (°K)
P (*atm* for (1) *or*
mm Hg for (2))

Different values of R can be obtained by utilizing the appropriate conversion factors.

Molar Volume ($\bar{V}$)

One mole of any gas at 273°K and 760 mm Hg will occupy 22.414 liters. This constant is obtained from the ideal gas law. From equation 2-5:

If: $P = 760$ mm Hg
$n = 1$ *mole*
$R = 62.4\ (\ell)\ (mm\ Hg)\ (g\text{-}mole)^{-1}(°K)^{-1}$
$T = 273°K$
$V = \bar{V}$ *(molar volume)*

$$P \times V = n \times R \times T$$

$$(760\ mm\ Hg)\ (V) = (1\ g\text{-}mole)(62.4\frac{\ell \cdot mm\ Hg}{g\text{-}mole\ °K})(273°K)$$

$$V = \frac{(1)(62.4)(273)}{760}\ \ell$$

$$V = 22.414\ell = \bar{V}$$

Therefore 1 *mole* of an ideal gas at 273°K and 760 mm Hg occupies 22.414ℓ. In other words, the molar volume ($\overline{V}$) of an ideal gas at 273°K and 760 mm Hg is *22.414 ℓ/mole*.

At *EPA standard conditions (760 mm Hg, 298°*K) one *mole* of any gas will occupy 24.46ℓ. The volume per *mole* constant for any gas at a given pressure and temperature is called the *molar volume* and is symbolized by $\overline{V}$.

Gas Density

Gas density can be determined by rearranging Equation 2-5 and letting density $\varrho = m/V$.

(Eq. 2-6)

$$PV = nRT = \frac{m}{M}RT$$

$$\frac{m}{V} = \varrho = \frac{PM}{RT}$$

Where:

ϱ = *density*
P = *absolute pressure*
M = *molecular weight*
T = *absolute temperature*
R = *universal gas constant*

Another method of determining density is by utilizing the fact that there are 24.46 liters per g-*mole* at 298°K and 760 mm Hg.

In the relationship, $\varrho = m/V$: if V is in terms of molar volume, $\overline{V}$ (ℓ/g-*mole* of a gas at STP), then m must be in terms of molecular weight, M (g/g-*mole*). So $\varrho = M/\overline{V}$ at a given temperature and pressure.

$$\varrho = \frac{M\dfrac{298}{T}\dfrac{P}{760}}{24.46}$$, *corrected to standard temperature and pressure conditions (STP)*

Where:

ϱ = *gas density* (g/ℓ)
M = *molecular weight* (g/g-*mole*)
24.46 = *molar volume* (ℓ/g-*mole*) *at standard conditions*
298 = *temperature* (°K) *at standard conditions*
T = *temperature* (°K) *at actual conditions*
760 = *pressure* (mm Hg) *at standard conditions*
P = *pressure* (mm Hg) *at actual conditions.*

Standard Conditions for Atmospheric Sampling

To be able to compare gas sampling data collected by various agencies and other organizations, all gas volumes must be corrected to a set of predetermined ("standard") conditions. For atmospheric or ambient sampling, these conditions are:

25 °C or 298 °K, and 760 mm Hg

The equation used to correct volumes sampled to standard conditions is:

(Eq. 2-7)

$$V_2 = (V_1)\left(\frac{P_1}{P_2}\right)\left(\frac{T_2}{T_1}\right)$$

$$V_2 = (V_1)\left(\frac{P_1}{760\text{ mm Hg}}\right)\left(\frac{298\,^\circ\text{K}}{T_1}\right)$$

$$V_2 = (V_1)(0.39)\left(\frac{P_1}{T_1}\right)$$

Where:

V_2 = *volume of gas at 2nd conditions or at* P_2 *and* T_2, ℓ
V_1 = *volume of gas at 1st conditions of* P_1 *and* T_1, ℓ
T_1 = *initial temperature of gas,* °K
T_2 = *final temperature of gas, in this case* = 298 °K
P_1 = *initial pressure of gas,* mm Hg
P_2 = *final pressure of gas, in this case* = 760 mm Hg

$$0.39 = \frac{298}{760}$$

Standard conditions for Temperature and Pressure are abbreviated STP.

Origin and Definition of Viscosity

Viscosity is the result of two phenomena: (a) intermolecular cohesive forces and (b) momentum transfer between flowing strata caused by molecular agitation perpendicular to the direction of motion. Between adjacent strata of a flowing fluid a shearing stress results that is directly proportional to the velocity gradient. (Figure 2-10). *Viscosity is often defined as resistance to flow.*

The relationship of these forces is shown in Equation 2-8.

(Eq. 2-8)

$$g_c \mathrm{T} = \mu \frac{dv}{dy}$$

Where:

g_c = *dimensional constant*
T = *unit shearing stress between adjacent layers of fluid*
$\frac{dv}{dy}$ = *velocity gradient*
μ = *proportionality constant (viscosity)*

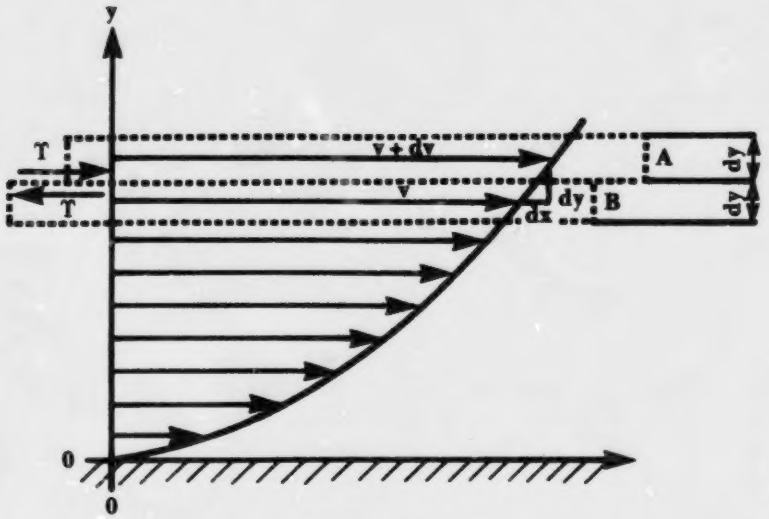


Figure 2-10. Velocity gradient.

The proportionality constant, μ, is called the coefficient of viscosity, or merely, *viscosity*. It should be noted that the pressure does not appear in Equation 2-8, indicating that the shear (Ƭ) and the viscosity (μ) are independent of pressure. (Viscosity actually increases very slightly with pressure but this variation is negligible in most engineering problems (2).)

Kinematic Viscosity

Kinematic viscosity is defined according to the following relationship:

(Eq. 2-9)

$$\nu = \frac{\mu}{\varrho}$$

Where:
ν = kinematic viscosity
μ = viscosity of the gas
ϱ = density of the gas (note the absence of dimensions of force)

Liquid Viscosity Versus Gas Viscosity

Liquid Viscosity

In a liquid, transfer of momentum between strata having different velocities is small, compared to the cohesive forces between the molecules. Hence, shear stress (Ƭ) is predominantly the result of intermolecular cohesion. Because forces of cohesion decrease with an increase in temperature, the shear stress decreases with an increase in temperature. Equation 2-8 shows that shear stress is directly proportional to the viscosity. Therefore, liquid viscosity decreases when the temperature increases

Gas Viscosity

In a gas, the molecules are too far apart for intermolecular cohesion to be effective. Thus, shear stress is predominately the result of an exchange of momentum between flowing strata caused by molecular activity. Because molecular activity increases with temperature increases, the shear stress increases with a rise in the temperature. Therefore, gas viscosity is increased when the temperature increases.

Determination of Viscosity of Gases

The viscosity of a gas may be found accurately from the following formula:

(Eq. 2-10)

$$\frac{\mu}{\mu^{\circ}} = \left(\frac{T}{273.1}\right)^{n}$$

Where:

μ = *viscosity at temperature* T (°K)
μ° = *viscosity at* 0°C *and prevailing pressure*
T = *absolute prevailing temperature* (°K)
n = *an empirical exponent* ($n = 0.768$ *for air*).

The viscosity of air and other gases at various temperatures and at a pressure of 1 atmosphere can be determined from the nomograph in Figures 2-11 and 2-12, or from Equation 2-10. The unit of the viscosity coefficient is the poise:
1 poise = gm/cm: sec. A centipoise (cp) is equal to 10^{-2} poise.

Reynold's Number

Definition

A typical inertial force per unit volume of fluid is

$$\frac{\varrho v^{2}}{g_{c} L}$$

A typical viscous force per unit volume of fluid is

$$\frac{\mu v}{g_{c} L^{2}}$$

The first expression divided by the second provides the dimensionless ratio known as Reynold's Number:

(Eq. 2-11)

$$N_{Re} = \frac{L v \varrho}{\mu} = \frac{\textit{inertial force}}{\textit{viscous force}}$$

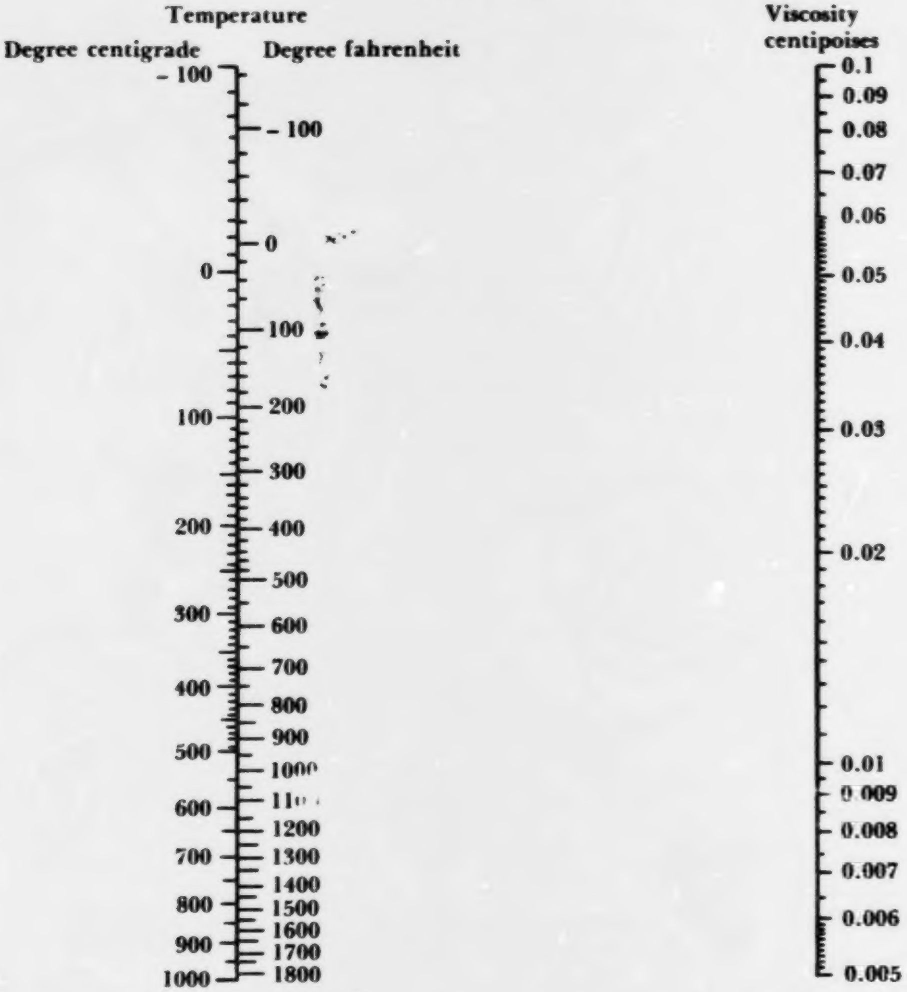
Where:

ϱ = *density of the fluid (mass/volume)*
v = *velocity of the fluid*
g_c = *dimensional constant*
L = *a linear dimension*
μ = *viscosity of the fluid*
N_{Re} = *Reynold's Number*

The larger the Reynold's Number, the smaller is the effect of viscous forces; the smaller the Reynold's Number, the greater the effect of the viscous forces.

The linear dimension, *L*, for flow through tubes and ducts is a length characteristic of the flow system. It is equal to four times the mean hydraulic radius, which is the cross-sectional area divided by the wetted perimeter. Thus for a circular pipe, $L =$ diameter of the pipe; for a particle settling in a fluid medium, $L =$ diameter of the particle; for a rectangular duct, $L =$ twice the length times the width divided by the sum; and for an annulus such as a rotameter system, $L =$ outer diameter minus the inner diameter.

Viscosity of air at 1 atmosphere *



(1)centipoise	$(10)^{-2}\ \frac{gm}{cm - sec}$ $(10)^{-2}$ poise	$2.09(10)^{-5}\ \frac{lb_f - sec}{ft^2}$	$2.09(10)^{-5}\ \frac{slug}{ft - sec}$	$6.72(10)^{-4}\ \frac{lb_m}{ft - sec}$

*Perry, J. H. Chemical Engineer's Handbook, McGraw-Hill Book Co., New York, 1950.

Figure 2-11. Viscosity nomograph for air.

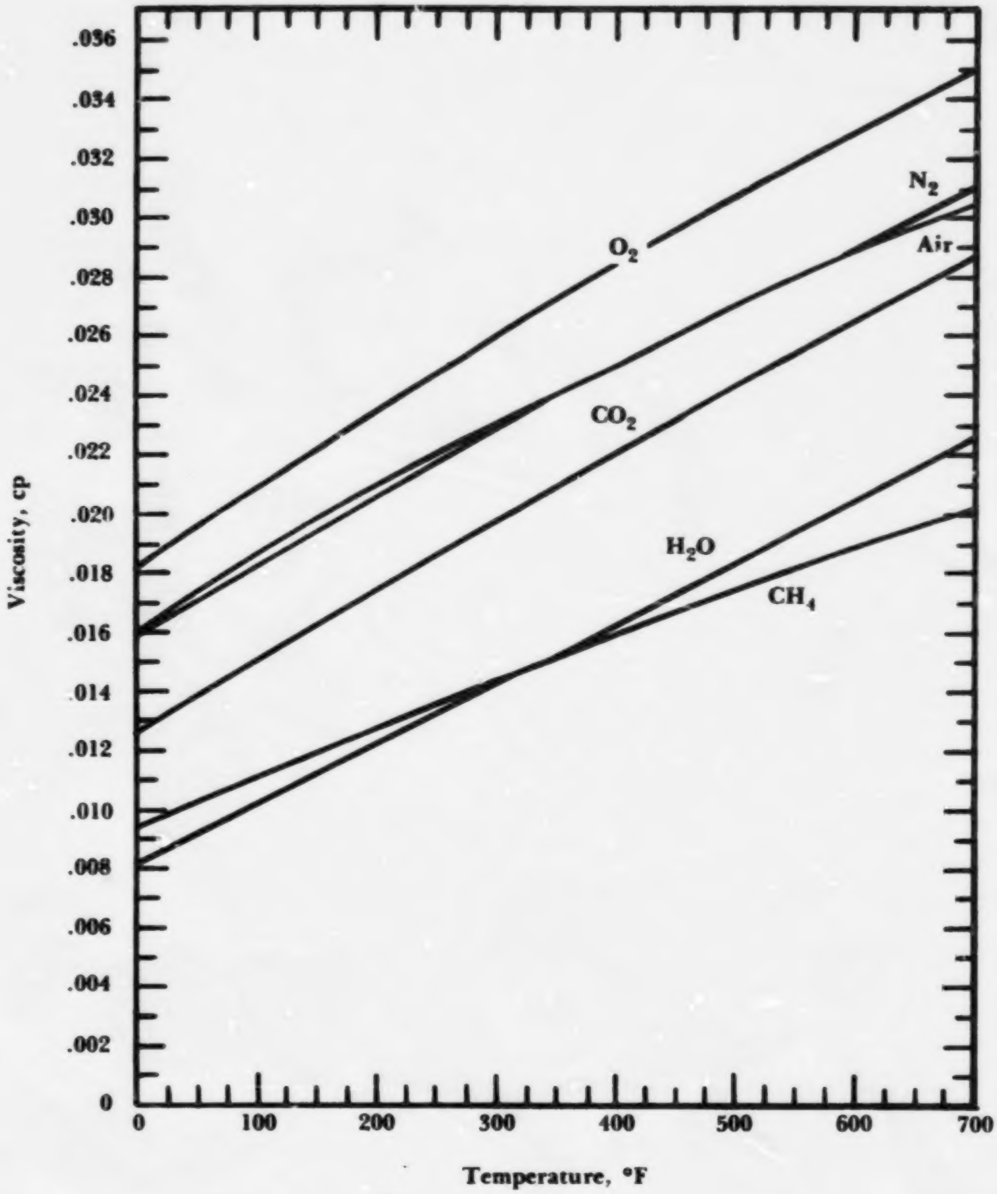


Figure 2-12. Viscosity nomograph of various gases at 1 atmosphere.

Laminar and Turbulent Flow

Laminar Flow

In laminar flow, the fluid is constrained to motion in layers (or laminae) by the action of viscosity. The layers of fluid move in parallel paths that remain distinct from one another; any agitation is of a molecular nature only. Laminar flow occurs when Reynold's Number is less than 0.1 for particles settling in a fluid medium.

Turbulent Flow

In turbulent flow, the fluid is not restricted to parallel paths but moves forward in a haphazard manner. Fully turbulent flow occurs when Reynold's Number is greater than 1000 for settling particles having diameters greater than 40μm in air with a 60% RH at 20°C.

Summary of Useful Equations

Temperature

$$°C = (°F - 32)/1.8$$
$$°F = 1.8°C + 32$$
$$°K = °C + 273$$

Where:
°F = degrees Fahrenheit
°C = degrees Centigrade or Celsius
°K = degrees Kelvin

Pressure

$$P = P_b + p_g$$

$$P = \varrho_f \left(\frac{g}{g_c}\right) h$$

$$\varrho_{f(1)} h_{f(1)} = \varrho_{f(2)} h_{f(2)}$$

$$1 \; std \; atm \equiv 29.92 \text{ in Hg}$$
$$\equiv 760 \text{ mm Hg}$$

Where:
P = *absolute pressure*
ϱ = *density*
h = *pressure head or height*
g = *gravitational acceleration*
g_c = *dimensional constant*

Subscripts
g = *gage*
f = *fluid*
b = *barometric or atmospheric*

Ideal Gas Law

$$PV = nRT$$

$$PV = \frac{m}{M} RT$$

$$R = \frac{0.08205 \text{ (liters)}(atm)}{(\text{g-}mole)(\text{°K})}$$

$$= \frac{62.4 \text{ (liters)(mm Hg)}}{(\text{g-}mole)(\text{°K})}$$

1 g-*mole* ≡ 22.414 liters at 273°K and 760 mm Hg (molar volume)

Where:
P = *absolute pressure*
V = *volume*
m = *mass*
M = *molecular weight*
R = *gas constant*
T = *absolute temperature*
n = *number of g-moles of a gas*

Gas Density

$$\varrho = \frac{PM}{RT}$$

Where:
ϱ = *density*
P = *absolute pressure*
R = *gas constant*
T = *absolute temperature*
M = *molecular weight*

Viscosity, μ

$$1\ cp \equiv 6.72 \times 10^{-4} \frac{\text{lb}_m}{\text{ft} \cdot \text{sec.}}$$

$$1\ poise = 1 \frac{\text{g}}{\text{cm} \cdot \text{sec}}$$

$$1\ cp = 10^{-2} \text{ poise}$$

Reynold's Number

$$N_{Re} = \frac{Lv\varrho}{\mu} = \frac{\text{inertial force}}{\text{viscous force}}$$

Where:

ϱ = *density of the fluid (mass/volume)*
v = *velocity of the fluid*
g_c = *dimensional constant*
L = *a linear dimension*
μ = *viscosity of the fluid*
N_{Re} = *Reynold's Number*

References

1. J. K. Uennard. *Elementary Fluid Mechanics.* New York: John Wiley and Sons, Inc., 1947.
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3. J. H. Perry. Chemical Engineers Handbook. New York: McGraw-Hill Book Co., Inc., 1950.
4. Robert P. Benedict. *Fundamentals of Temperature, Pressure, and Flow Measurements.* New York: John Wiley and Sons, Inc., 1969.
5. William H. Nebergall, Frederic C. Schmidt, and Henry F. Holtzclaw, Jr. *General Chemistry,* Lexington, MA: Reytheon Education Company, 1968.

Units of Measurement

Recommended Units (Reference 1)

"At the present time, personnel engaged in the study of air pollution are confronted with a multitude of confusing and conflicting units of expression. A search through the literature has shown a wide variation in the methods of reporting data. Many of the units of expression are carry-overs from other fields, such as water pollution studies and industrial hygiene surveys. While these methods of expression are not incorrect, their application to air pollution studies is often misleading."

This section of the manual covers the units presently being used and those recommended for the more commonly measured air pollution parameters.

The recommended units were selected so that the reported values would be small whole numbers in the metric system. If possible, the reported units should be the same as those that are actually measured. For example, weight should be reported in grams or milligrams, and volume in cubic meters. The measured value should never be multiplied by large numbers to extrapolate to extremely large areas or volumes. If this is done, the resulting values are misleading. For example: to report particulate fallout on a weight per square mile basis, the area actually sampled, which is about 1 square foot, would have to be extrapolated to a square mile by multiplying the measured results by almost 28,000,000. Reporting the results on the basis of a square mile is misleading, because we are saying that the one square foot that we sampled is representative of a square mile surrounding this sampling site. This we know, in most cases, is not true.

When reporting results, the type of sampling instrument should be described, and when volumes of air are sampled, the temperature and pressure at the time of the sampling should be reported.

Particle Fallout

Units Presently In Use

- Tons per square mile per month
- Tons per square mile per year
- Pounds per acre per month
- Pounds per acre per year
- Pounds per thousand square feet per month
- Ounces per square foot per month
- Grams per square foot per month
- Grams per square meter per month
- Kilograms per square kilometer per month
- Grams per month per 4-inch or 6-inch jar
- Milligrams per square inch per month

Recommended Units

Milligrams per square centimeter per time interval as mg/cm^2/mo, or mg/cm^2/yr.

Ranges Reported

0.5 to 135 mg/cm^2/mo.

Outdoor Airborne Particulate Sampling

Units Presently In Use

- Milligrams per cubic meter
- Parts per million by weight
- Grams per cubic foot
- Grams per cubic meter
- Micrograms per cubic meter
- Micrograms per cubic foot
- Grams per cubic foot
- Pounds per thousand cubic foot

Recommended Unit

Micrograms per cubic meter at standard temperature and pressure.

Ranges Expected

10 to 5000 micrograms per cubic meter.

Gaseous Materials

Units Presently In Use

- Milligrams per cubic meter
- Micrograms per cubic meter
- Micrograms per liter
- Parts per million (ppm) by volume
- Parts per hundred million
- Parts per billion (ppb) by volume
- Parts per trillion (ppt) by volume
- Ounces per cubic foot
- Pounds per cubic foot
- Grams per cubic foot
- Pounds per thousand cubic foot

Recommended Unit

ppm or ppb by volume

Ranges Reported

Parts per trillion to parts per million.

Standard Conditions for Reporting Gas Volumes

Units Presently In Use

- 760 millimeters Hg pressure and 20°C
- 760 millimeters Hg pressure and 0°C
- 760 millimeters Hg pressure and 65°F
- 760 millimeters Hg pressure and 25°C
- 700 millimeters Hg pressure and 0°C
- 700 millimeters Hg pressure and 20°C
- 30 inches of mercury pressure and 65°F

Recommended Units

760 millimeters Hg pressure and 25°C.

Particle Counting

Units Presently In Use

- Number per cubic meter of gas
- Number per liter of gas
- Number per cubic centimeter of gas
- Number per cubic foot of gas

Recommended Units

Number of particles per cubic meter of gas

Range Reported

10 million and above particles per cubic meter.

Particle Count In Sedimentation Devices

(both horizontal and vertical)

Recommended Units

Number of particles per square centimeter per time interval.

Temperature

Units Presently In Use

- Degrees Celsius or Centigrade
- Degrees Fahrenheit

Recommended Unit

Degrees Celsius or Centigrade (°C)

Time

It is recommended that time be measured on the 0000 to 2400 basis to eliminate the possible confusion that results from two 12-hour (a day) sections. Example: 1:00 a.m. = 0100, 1:00 p.m. = 1300, 12:00 midnight = 0000.

Pressure

Units Presently In Use

Atmospheric Pressure
- Atmospheres
- Millimeters of mercury
- Inches of mercury

Sampling Pressures
- Millimeters of mercury
- Inches of mercury
- Millimeters of water
- Inches of water

Recommended Unit

Millimeters of mercury (mm Hg)

Sampling Rates

Units Presently In Use

- Cubic meters per second
- Cubic meters per minute
- Cubic feet per second
- Cubic feet per minute
- Liters per second
- Liters per minute
- Cubic centimeters per second
- Cubic centimeters per minute

Recommended Units

- Cubic meters per minute
- Cubic centimeters per minute

Ranges Reported

Cubic centimeters per minute to 3 cubic meters per minute. The selection of cubic meters, or cubic centimeters, will depend on the sampling equipment used: the units chosen should give small whole numbers.

Visibility

Units Presently In Use

- Miles and fractions of a mile
- Kilometers and fractions of kilometers

Recommended Unit

Kilometers

Summary of Recommended Units

- *Particle fallout*. Milligrams per square centimeter per time interval.
- *Outdoor airborne particulates*. Micrograms per cubic meter at STP.
- *Gaseous material*. ppm or ppb by volume.
- *Gas volumes* reported at STP (760 millimeters Hg pressure and 25°C).
- *Particle count on sedimentation devices*. Number of particles per square centimeter per time interval.
- *Temperature*. Centigrade scale.
- *Time*. 0000 to 2400 hours per day.
- *Pressure*. Millimeters of mercury.
- *Sampling rates*. Cubic meters per minute, or cubic centimeters per minute.
- *Visibility*. Kilometers.

  It is believed that adoption and use of the recommended units of expression will result in more uniform reporting and will remove much of the confusion that is now found in reports of air pollution.

Conversions

Until a unform system of units has been agreed upon and adhered to in the scientific literature, conversion from one unit of expression to another will be a necessity.

Sample Particulate Problem:

Convert 89.0 tons per square mile to the recommended units (milligrams per square centimeter).

Solution:

$$89.0\,\frac{\text{tons}}{\text{mi}^2} \times \frac{2000\ \text{lb}}{\text{ton}} \times \frac{453.6 \times 10^3\ \text{mg}}{\text{lb}} \times \frac{\text{mi}^2}{(5280)^2\text{ft}^2} \times \frac{\text{ft}^2}{(12)^2\text{in}^2} \times \frac{\text{in}^2}{(2.54)^2\text{cm}^2} = \frac{3.2\ \text{mg}}{\text{cm}^2}$$

Sample Gas Problem:

Discussion:

The expression parts per million is without dimensions, i.e., no units of weight or volume are specifically designed. Using the format of other units, the expression may be written:

$$\frac{\text{parts}}{\text{million parts}}$$

"Parts" are not defined. If cubic centimeters replace parts, we obtain:

$$\frac{\text{cubic centimeters}}{\text{million cubic centimeters}}$$

Similarly, we might write pounds per million pounds, tons per million tons, or liters per million liters. In each expression, identical units of weight or volume appear in both the numerator and denominator and may be cancelled out, leaving a dimensionless term.

An analog of parts per million is the more familiar term "percent." Percent can be written:

$$\frac{\text{parts}}{\text{hundred parts}}$$

To convert from part per million by volume, ppm_v, $(\mu\ell/\ell)$ it is necessary to know the molar volume at the given temperature and pressure and the molecular weight of the pollutant.

At 25°C and 760 mm Hg, one mole of any gas occupies 24.46 liters.

Convert the following:

2.5 ppm by volume of SO_2 was reported as the atmospheric concentration.

a. What is this concentration in micrograms (μg) per cubic meter (m^3) at 25°C and 760 mm Hg?

b. What is the concentration in $\mu g/m^3$ at 37°C and 752 mm Hg?

Solution:

Let parts per million equal $\mu\ell/\ell$ then 2.5 ppm $= 2.5^{\mu\ell}/\ell$. The molar volume at 25° and 760 mm Hg is 24.46ℓ and the molecular weight of SO_2 is 64.1 g/mole.

$$\text{a. } \frac{2.5\ \mu\ell}{\ell} \times \frac{1\ \mu\text{mole}^*}{24.46\ \mu\ell} \times \frac{64.1\ \mu g}{\mu\text{mole}} \times \frac{1000\ \ell}{m^3} = 6.5 \times 10^3\ \frac{\mu g}{m^3} \text{ at STP}$$

$$\text{b. } (24.46\ \mu\ell)\left(\frac{310\,^\circ K}{298\,^\circ K}\right)\left(\frac{760\text{ mm Hg}}{752\text{ mm Hg}}\right) = 25.73\ \mu\ell$$

$$\frac{2.5\ \mu\ell}{\ell} \times \frac{1\ \mu\text{mole}}{25.73\ \mu\ell} \times \frac{64.1\ \mu g}{\mu\text{mole}} \times \frac{1000\ \ell}{m^3} = 6.2 \times 10^3\ \frac{\mu g}{m^3} \text{ at 37°C, 752 mm Hg}$$

This sample problem also points out the need for reporting temperature and pressure when the results are presented on a weight to volume basis.

*since, at STP 1 mole of a gas occupies 24.46 liters, 1 μmole $= 24.46\ \mu\ell$.

Problems

1. Convert the following:
   a. 68 °F → °C (answer 20 °C)
   b. 28 °C → °K (answer 301 °K)
   c. 29.03 in Hg → mm Hg (answer 737.3 mm Hg)
2. An ideal gas occupies a volume of 2000 mℓ at 700 mm Hg and 20 °C. What is the volume of the gas at STP? (answer 1874 mℓ)
3. If a concentration of carbon monoxide (CO) is noted as 10 ppm, what is this concentration in terms of μg/m^3 at STP? (CO = 28 g/mole) (answer 11,440 μg/m^3, 11.4 mg/m^3)
4. Ambient air was sampled at a rate of 2.25 liters per minute for a period of 3.25 hours at 19 °C, 748 mm Hg. What volume of air was sampled at STP? (answer 441 ℓ)
5. Convert 1000 μg/m^3 SO$_2$ at STP to ppm. (SO$_2$ = 64 g/mole) (answer 0.38 ppm)

Tables to use in this task appear in Appendix C of this manual.

References

1. Terraglio, F. P., Sheehy, J. P., and Manganelli, R. M. *Recommended Units of Expression for Air Pollution. J. Air Poll. Control Assoc.* 8:220-222, 1958.
2. Weast, R. C., and Astle, M. J. *Handbook of Chemistry and Physics*, Boca Raton, Florida: Chemical Rubber Publishing Co., 60th edition, 1979.

Definitions

Air at EPA Standard Conditions	Air at 25°C and 760 mm Hg (29.92 in. Hg).
Air Pollution	The presence of unwanted material in the air. The term "unwanted material" here refers to material concentrations present for a sufficient time and under circumstances to interfere significantly with comfort, health, or welfare of persons, or with the full use and enjoyment of property.
Arrester	A term for an air cleaning device.
Aspirator	Any apparatus such as a squeeze bulb, fan, pump, or venturi, that produces a movement of a fluid by suction.
Atmosphere, The	The whole mass of air surrounding the earth and being composed largely of oxygen and nitrogen.
Atmosphere, An	A specific gaseous mass, occurring either naturally or artificially containing any number of constitutents and in any proportion.
Breathing Zone	That location in the atmosphere at which persons breathe.
Chimney Effect	A phenomenon consisting of a vertical movement of a localized mass of air or other gases due to temperature differences.
Collection Efficiency	The percentage of a specified substance retained by a gas cleaning or sampling device.
Collector	A device for removing and retaining contaminants from air or other gases. Usually this term is applied to cleaning devices in exhaust systems.
Cloud	A visible dispersion occupying a discrete portion of space, with apparent boundaries.
Condensate	Liquid or solid matter formed by condensation from the vapor phase. In sampling, the term is applied to the components of an atmosphere that have been isolated by simple cooling.
Condensation	The process of converting a material in the gaseous phase to a liquid or solid state by decreasing temperature, by increasing pressure, or both. Usually in air sampling only cooling is used.
Condensoid	The particles of a dispersion formed by condensation.
Contaminant	Unwanted material.
Count Median Size	A measurement of particle size for samples of particulate matter, consisting of that diameter of particle such that one half of the number of particles is larger and half is smaller

Density	The mass per unit volume of substance.
Diffusion, Molecular	A process of spontaneous intermixing of different substances, attributable to molecular motion and tending to produce uniformity of concentration.
Dispersion	The most general term for a system consisting of particulate matter suspended in air or other gases.
Dispersoid	The particles of a dispersion.
Diurnal	The term means recurring daily. Applied to (variations in concentration of) air contaminants, diurnal indicates variations following a distinctive pattern and recurring from day to day.
Dust	A loose term applied to solid particles predominantly larger than colloidal and capable of temporary suspension in air or other gases. Dusts do not tend to flocculate except under electrostatic forces; they do not diffuse but settle under the influence of gravity. Derivation from larger masses through the application of physical force is usually implied.
Dust Fall	See Particle Fall.
Dust Loading	An engineering term for "dust concentration," usually applied to the contents of collection ducts and the emission from stacks.
Droplet	A small liquid particle of such size and density as to fall under still conditions, but which may remain suspended under turbulent conditions.
Efficiency	The ratio of attained performance to absolute performance, commonly expressed in percent.
Efficiency, Fractional	The mean collection efficiency for specific size fractions of a contaminant. Commonly this term has been applied to the performance of air cleaning equipment towards particulate matter in various size ranges.
Ejector	A device that uses a fluid under pressure, such as steam, air, or water, to move another fluid by developing suction. Suction is developed by discharging the fluid under pressure through a venturi.
Emissions	The total of substances discharged into the air from a stack vent, or other discrete source.
Emission Mixture	The total mixture in the outside atmosphere of emission from all sources.
Flocculation	Synonymous with agglomeration.
Flowmeter	An instrument for measuring the rate of flow of a fluid moving through a pipe or duct system. The instrument is calibrated to give volume or mass rate of flow.

Fly Ash	The finely divided particles of ash entrained in flue gases arising from the combustion of fuel. The particles of ash may contain incompletely burned fuel. The term has been applied predominantly to the gas-born ash from boilers with spreader stoker, underfeed stoker, and pulverized fuel (coal) firing.
Fog	A loose term applied to visible aerosols in which the dispersed phase is liquid. Formation by condensation is usually implied; in meterology, a dispersion of water or ice.
Freezing Out	See Sampling, Condensation.
Fume	Properly, the solid particles generated by condensation from the gaseous state, generally after volatilization from melted substances, and often accompanied by a chemical reaction such as oxidation. Fumes flocculate and sometimes coalesce. Popularly, the term is used in reference to any of all types of contaminant, and in many laws or regulations with the added qualification that the contaminant have some unwanted action.
Gas	One of the three states of aggregation of matter, having neither independent shape nor volume and tending to expand indefinitely.
Grab Sample	See Sampling, Instantaneous.
Impaction	A forcible contact of particles of matter, a term often used synonymously with impingement.
Impactor	A sampling device that employs the principle of impaction (impingement). The "cascade impactor" refers to a specific instrument employing several impactions in series to collect successively smaller sizes of particles.
Impingement	The act of bringing matter forcibly in contact. As used in air sampling, impingement refers to a process for the collection of particulate matter in which the gas being sampled is directed forcibly against a surface.
Impingement, Dry	The process of impingement carried out so that particulate matter carried in the gas stream is retained upon the surface against which the stream is directed. The collecting surface may be treated with a film of adhesive.
Impingement, Wet	The process of impingement carried out within a body of liquid, the latter serving to retain the particulate matter.
Impinger	Broadly, a sampling instrument employing impingement for the collection of particulate matter. Commonly, this term is applied to specific instruments, the "midget" and "standard" impinger.

Impinger, Midget	A specific instrument employing wet impingement, using a liquid volume of 10 ml and a gas flow of 0.1 cu. ft. per min. (Note: See J. R. Littlefield, E. L Feicht, and H. H. Schrenk, "Midget Impinger for Dust Sampling," U.S. Bureau of Mines. Report of Investigations 3360 (1937).)
Impinger, Standard	A specific instrument employing wet impingement, using a liquid volume of 75 ml and a gas flow of 1 cu. ft. per min. (Note: See L. Greenburg and G. W. Smith, "A New Instrument for Sampling Aerial Dust," U.S. Bureau of Mines, Report of Investigations 2392 (1922). See also T. Hatch, H. Warren, and P. Drinker, Journal Industrial Hygiene, No. 14, p. 301 (1932).)
Isokinetic	A term describing a condition of sampling, in which the flow of gas into the sampling device (at the opening or face of the inlet) has the same flow rate and direction as the gas stream being sampled.
Mass Concentration	Concentration expressed in terms of mass of substance per unit volume of gas or liquid.
Mass Median Size	A measurement of particle size for samples of particulate matter, consisting of that diameter such that the mass of all larger particles is equal to the mass of all smaller particles.
Mist	A loose term applied to dispersions of liquid particles, the dispersion being of low concentration and the particles of large size. In meteorology, a light dispersion of water droplets of sufficient size to be falling.
Month	For reporting analyses of outdoor air on a monthly rate results are calculated to a base of 30 days.
Odor	That property of a substance affecting the sense of smell; any smell; scent; perfume.
Odor Concentration	The number of unit volumes that a unit volume of sample will occupy when diluted to the odor threshold.
Odor Unit	Unit volume of air at the odor threshold.
Odorant	Odorous substance.
Orifice Meter	A flowmeter, employing as the measure of flow rate the difference between the pressures measured on the upstream and downstream sides of the orifice (that is, the pressure differential across the orifice) in the conveying pipe or duct.
Particle	A small discrete mass of solid or liquid matter.

Particle Concentrations	Concentration expressed in terms of number of particles per unit volume of air or other gas. (Note: On expressing particle concentration, the method of determining the concentration should be stated.)
Particle Fall	A measurement of air contamination consisting of the mass rate at which solid particles deposit from the atmosphere. A term used in the same sense as the older terms Dust Fall and Soot Fall but without any implication as to nature and source of the particles.
Particle Size	An expression for the size of liquid or solid particles expressed as the average or equivalent diameter.
Particle Size Distribution	The relative percentage by weight or number of each of the different size fractions of particulate matter.
Precipitation, Electrostatic	A process consisting of the separation of particulate matter from air or other gases under the influence of an electrostatic field.
Precipitation, Meteorological	The precipitation of water from the atmosphere in the form of hail, mist, rain, sleet, and snow. Deposits of dew, fog, and frost are excluded.
Precipitation, Thermal	A process consisting of the separation of particulate matter from air and other gases under the influence of a relatively large temperature gradient extending over a short distance. In the "Thermal Precipitator" (a sampling instrument), the air or gas is drawn through a narrow chamber across which extends a heated wire, particulate matter being deposited upon the adjacent collecting surface.
Precipitation, Ultrasonic	A process consisting of the separation of particulate matter from air and other gases following agglomeration induced by an ultrasonic field.
Precipitator, Electrostatic	Apparatus employing electrostatic precipitation for the separation of particles from a gas stream. The apparatus may be designed either for sampling or for cleaning large volumes of gas.
Precision	The degree of agreement of repeated measurements of the same property, expressed in terms of dispersion of test results about the mean result obtained by repetitive testing of a homogenous sample under specified conditions. The precision of a method is expressed quantitatively as the standard deviation computed from the results of a series of controlled determinations.
Pressure Static	The pressure of a fluid at rest, or in motion, exerted perpendicularly to the direction of flow.

Pressure, Velocity	That pressure caused by and related to the velocity of the flow of fluid; a measure of the kinetic energy of the fluid.
Pressure, Total	The pressure representing the sum of static pressure and velocity pressure at the point of measurement.
Pressure, Gage	The difference in pressure existing within a system and that of the atmosphere. Zero gage pressure is equal to atmospheric pressure.
Probe	A tube used for sampling or for measuring pressures at a distance from the actual collection or measuring apparatus. It is commonly used for reaching inside stacks and ducts.
Rotameter	A device, based on the principle of Stoke's Law, for measuring rate of fluid flow. It consists of a tapered vertical tube having a circular cross-section, and containing a float that is free to move in a vertical path to a height dependent upon the rate of fluid flow upward through the tube.
Sample, Integrated	A sample obtained over a period of time with (1) the collected atmosphere being retained in a single vessel, or (2) with a separated component accumulating into a single whole. Examples are dust sampling in which all the dust separated from the air is accumulated in one mass of fluid; the absorption of acid gas in an alkaline solution; and collection of air in a plastic bag or gasometer. Such a sample does not reflect variations in concentration during the period of sampling.
Sample, Continuous	Withdrawal of a portion of the atmosphere over a period of time with continuous analysis or with separation of the desired material continuously and in a "linear" form. Examples are continuous withdrawal of the atmosphere accompanied by absorption of a component in a flowing stream of absorbent or by filtration on a moving strip or paper. Such a sample may be obtained with a considerable concentration of the contaminant but it still indicates fluctuations in concentration that occur during the period of sampling.
Sampling	A process consisting of the withdrawal or isolation of a fractional part of a whole. In air or gas analysis, the separation of a portion of an ambient atmosphere with or without the simultaneous isolation of selected components.
Sampling, Condensation	A process consisting of the collection of one or several components of a gaseous mixture by simple cooling of the gas stream in a device that retains the condensate.

Sampling, Continuous	Sampling without interruptions throughout an operation or for a predetermined time.
Sampling, Instantaneous	Obtaining a sample of an atmosphere in a very short period of time such that this sampling time is insignificant in comparison with the duration of the operation or the period being studied.
Sampling, Intermittent	Sampling successively for limited periods of time throughout an operation or for a predetermined period of time. The duration of sampling periods and of the intervals between are not necessarily regular and are not specified.
Series Collection	An operation involving the use of two or more collectors joined in a series.
Settling Velocity	The terminal rate of fall of a particle through a fluid as induced by gravity or other external force; the rate at which frictional drag balances the accelerating force (or the external force).
Smog	A term derived from smoke and fog, applied to extensive atmospheric contamination by aerosols, these aerosols arising partly through natural processes and partly from the activities of human subjects. Now sometimes used loosely for any contamination of air.
Smoke	Small gas-borne particles resulting from incomplete combustion, consisting predominantly of carbon and other combustible material, and present in sufficient quantity to be observable independently of the presence of other solids.
Soot	Agglomerations of particles of carbon impregnated with "tar," formed in the incomplete combustion of carbonaceous material.
Sorbent	A liquid or solid medium in or upon which materials are retained by absorption or adsorption.
Sorption	A process consisting of either absorption or adsorption or both.
Specific Gravity	The ratio of the density of the substance in question to the density of a reference substance at specified conditions of temperature and pressure.
Temperature, Absolute	(a) Temperature measured on the thermodynamic scale, designated as degrees Kelvin (°K). (b) Temperature measured from absolute zero (-273.15°C or -459.67°F). The numerical values are the same for both the Kelvin scale and the ideal gas scale.

Vapor	The gaseous phase of matter which normally exists in a liquid or solid state.
Volume Concentration	Concentration expressed in terms of gaseous volume of substance per unit volume of air or other gas usually expressed in percent or parts per million.
Week	For reporting analyses of outdoor air on a weekly rate results are calculated to a base of 7 consecutive 24-hour days.
Year	For reporting analyses of outdoor air on a yearly rate twelve 30-day months are to be used.

Chapter 3

Air Measuring Instruments

Introduction to Air Movers

The primary purpose of an air mover in the sampling process is to create a flow of air that will allow the contaminant in the air to be analyzed directly or to be captured by a collection device for subsequent analysis. Collection devices include filters, impingers, and impactors (1). Air movers range in capacity from a few cubic centimeters per minute (cm^3/min) of air up to tens of cubic meters per minute (m^3/min). In operational complexity air movers range from a squeeze bulb to a multistage pump.

Relationship of Air Movers to Other Sampling System Components

Air movers are vital components of sampling trains used for the sampling and analysis of air for its pollutant content (see Figure 3-1). Several of the considerations governing the selection of an air mover for a particular application will be mentioned in this discussion.

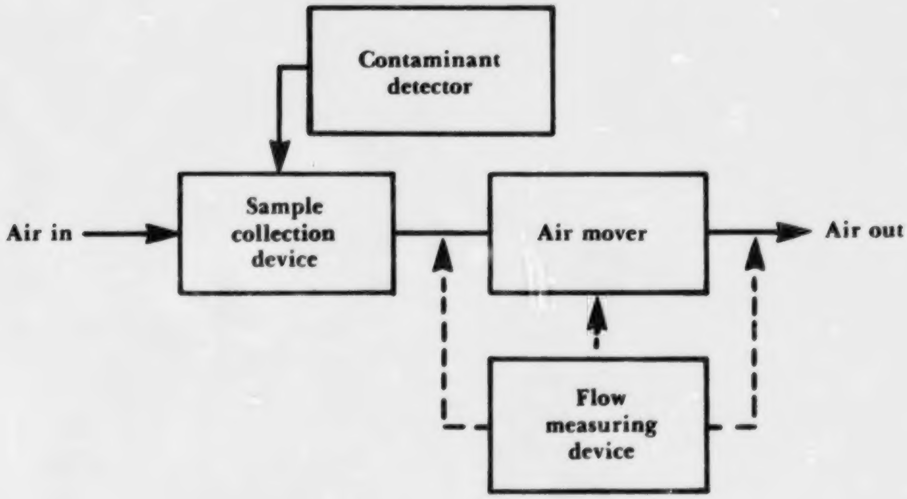


Figure 3-1. A sampling train.

Air Mover Classification

There are many parameters by which air movers can be evaluated and classified. Classification of air movers can be made according to their function, capacity, "driving" force, principle of operation, among other parameters. The classification scheme often depends to a great extent on the classifier. The actual types of air movers to be discussed are *pumps*, *ejectors*, *liquid displacers*, and *evacuated flasks*.

Air Mover Selection Criteria

Since there is no one "typical" air sampling train, equipment selection is an important aspect of any airborne sampling scheme, meaning that air mover selection must be made along with the selection of other sampling train components. Here are some of the many factors to be considered before selection will be discussed. The itemizing of the considerations is not necessarily in order of their importance.

Pollutant Concentration and Sampling Time

The required flow rate of the air mover is often determined by the sensitivity of the analysis method, which in turn sets the minimum quantity of the contaminant required for analysis (2). For example, if the analysis procedure required 10 μg of material to obtain the desired precision, and if the air contains 1 $\mu g/m^3$ of that material, a sample size of 10 m^3 would be required, assuming 100% collection efficiency. The required flow rate of the air mover can be calculated by determining the available sampling time and the sample volume required. For example, if the above-mentioned 10 m^3 of air had to be moved (sampled) in a period of 10 hours, an air mover of 1 m^3/hr capacity could be used. In many instances it is more feasible to sample for longer periods of time, and sometimes at higher rates, than those required. As long as the sample size is greater than the minimum detectable and less than the concentration that theoretically saturates the collection medium, this may be of no consequence.

Sampling Rate Required

In some instances it may be necessary to sample at some required flow rate to ensure efficient sample collection. An example is the collection of a sample by using a chemical reaction. The reaction kinetics may depend upon the length of time the contaminant is in the presence of the reacting substance, and the length of contact time is dependent on the sampling rate. Other examples include the collection of particulates by use of impingers or impactors. The particle size collected will be dependent on the approach velocities, and these in turn are dependent upon the sampling rates.

Physical and Chemical Nature of Air to be Sampled

The operation of the air mover selected must be compatible with the physical and chemical characteristics of the air and contaminant to be sampled. Air of a corrosive or abrasive nature can create problems with the air mover unless the internal parts are nonreactive with the sample air.

In instances where sampling is to be done in an environment of a potentially explosive nature, approved explosion-proof air movers or explosion-sealed air movers should be selected. A completely sealed electric motor for a pump (1), in conjunction with non-sparking metal parts, is an example of an explosion-sealed air mover.

Portability of Air Mover

Much air sampling is performed at temporary sampling sites. When sampling trains must be moved from location to location it is important that each component be as portable and light-weight as possible. At permanent sampling locations air mover portability is not such an important consideration.

The power source for the air mover may be the limiting factor in its portability, especially when the power source must be AC line voltage.

Air Mover Noise

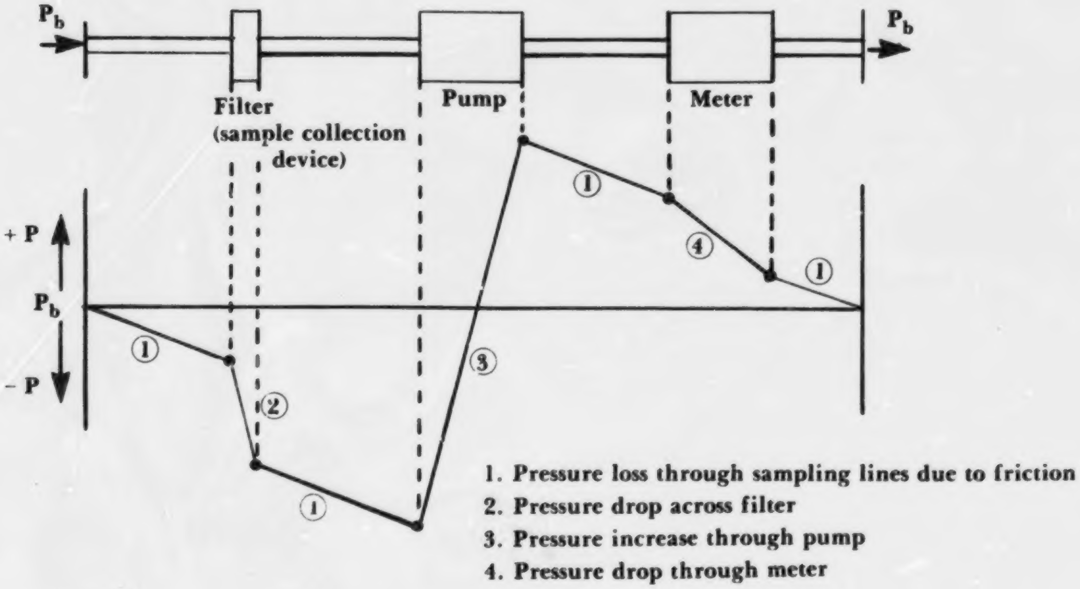
Since air sampling may be required in areas having noise restrictions, the noise produced by an air mover must be considered. Also, the suppression of air mover noise has aesthetic values. Noise levels may be considered in relation to the length of the sampling period, that is, for short periods high noise levels *may* be acceptable. Many commercially available air movers have special sound-adsorbing liners, vibration-reducing cushioning material, or mufflers as noise-reducing components of the mover itself.

Air Mover Maintenance

It is an established fact that man-made equipment, whether air sampler components or computers, will not be maintenance-free. Maintenance considerations are of special importance for equipment to be used in the field, because valuable time can be lost in transit between the repair shop and the sampling location. There are three particular points to consider about air mover maintenance: (a) air mover parts that might need repairing should be easily accessible; (b) the complete repair should not be very time consuming; and (c) air mover parts should not be overly expensive. Many costly breakdowns can be avoided if the proper preventative maintenance schedule is used.

Resistance

Flow resistance considerations may dictate the selection of an air mover of a particular type (see Figure 3-2). The sample collection device will offer some resistance to the flow of air through it; therefore, the air mover must be able to overcome this resistance so that efficient sample collection can be accomplished.



P_b
P_b
Filter (sample collection device)
Pump
Meter
+ P
P_b
− P
①
②
③
④
1. Pressure loss through sampling lines due to friction
2. Pressure drop across filter
3. Pressure increase through pump
4. Pressure drop through meter

Figure 3-2. Pressure profile for basic sampling apparatus.

Constant Flow Rate

It is often desirable to collect a sample at a constant flow rate. Variation in sample conditions or other external influences can make this difficult. For example, the resistance of a filter can be expected to increase with sample "buildup," thereby decreasing the flow rate through the sample apparatus. Poor voltage regulation can result in variable motor speeds leading to variable sampling rates (3). However, some commercially available air movers feature constant flow rates despite varying sampling conditions; others require flow regulation devices in order to have constant flow rates. Some flow regulation mechanisms will be discussed later in the chapter. Another factor of importance in some applications is the ability to vary the flow rate of the air mover and then to maintain constancy at the selected rate. This topic will also be discussed in more detail later.

Pumps

Pumps have been defined as devices that raise or transfer fluids (2). Since air is a fluid, a pump that moves air either raises it to another level or transfers it to another location. In air sample collection, the air is transferred from one location through, or into, a sample collection device.

Classification of Pumps

Categorization of pumps is a difficult task because of the many variables. This section will discuss pumps in terms of two broad classes based on flow variation with pressure. These two major classes will be subdivided into categories according to specific principles of operation: (a) *positive displacement pumps* and (b) *centrifugal pumps*.

Positive Displacement Pumps

Positive displacement pumps are often characterized by a linear relationship between the suction pressure and pump capacity (see Figure 3-3). This indicates that $\Delta Q / \Delta p$ (ΔQ is the change in flow rate; Δp is the pressure drop across the pump) is a constant value. Figures 3-3 and 3-5 are representative of characteristic curves of pumps to be discussed later.

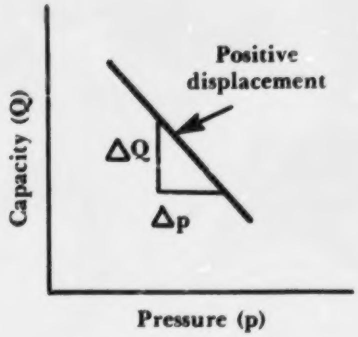


Figure 3-3. Positive displacement pump.

The name positive displacement arises from the fact that the inner parts of these pumps are movable and tight-fitting, and the air is displaced through them by the movement (displacement) of these tight parts (4). Figure 3-4 indicates a further subdivision of positive displacement pumps, this division being made according to the principle of operation. Reciprocating pumps are characterized by fixed casings containing movable pistons that work only forward-and-backward or up-and-down, and by the pressure of suction and discharge valves.

Principle of Operation	Type of Pump
Reciprocating	piston plunger diaphragm
Rotary (not discussed in this manual)	gear lobe vane screw rotary plunger

Figure 3-4. Classification of positive displacement pumps.

The operation of some of the specific types of reciprocating pumps will be discussed later in this section.

Centrifugal Pumps

Centrifugal pumps are representative of pumps other than positive displacement pumps. Centrifugal pumps do not have a straight line relationship between suction pressure and capacity, thus $\Delta Q/\Delta p$ is not constant (see Figure 3-5).

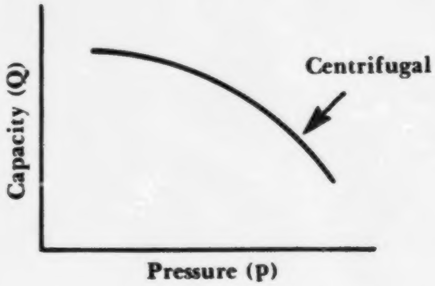


Figure 3-5. Centrifugal pump.

A centrifugal pump moves fluids by a centrifugal force created by a wheel, called an impeller, revolving in a tight casing (4). Some additional examples of pumps other than positive displacement pumps are: (a) turbine pumps, (b) propeller pumps, and (c) screw drag pumps. Each of these exhibit the same general pressure-capacity relationship as the centrifugal pump.

Positive Displacement Pump Operation

Some of the positive displacement pumps previously classified will now be discussed.

Piston Pumps (Reciprocating)

The principle of operation of a piston pump is that air is drawn into a chamber or cylinder on the suction stroke of a piston and then is pushed out on the discharge stroke (5), as illustrated in Figure 3-6. On the suction stroke the suction valve is open, allowing air to flow in; on the discharge stroke the suction valve closes and the discharge valve opens, allowing air to flow out. An internal combusion engine is an example of a piston pump. Piston pumps vary in complexity of operation from manually operated ones to models with many working parts.

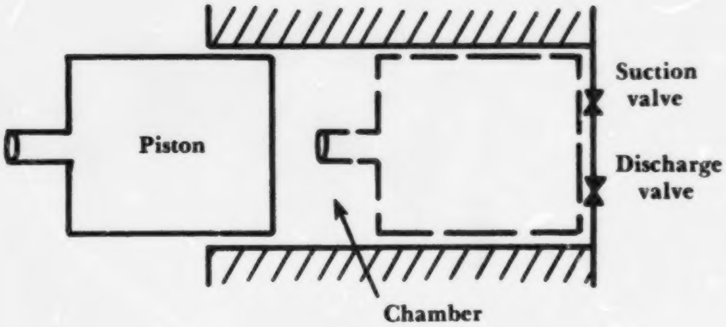


Figure 3-6. Piston pump.

Diaphragm Pumps (Reciprocating)

The operation of a diaphragm pump is very similar to a piston pump in principle. The piston (plunger) in a diaphragm pump does not move in a tightly-fitted chamber as in the piston pump, but is attached to the center of a circular diaphragm, the outer edge of which is bolted to a flange on the pump casing (6). The diaphragm may be made of metal (7) or some soft material such as Teflon® or neoprene (12). The most important characteristic of the diaphragm material is its flexibility and resistance to reaction with the air being moved. The up-and-down motion of the plunger is permitted by diaphragm flexibility without the rubbing of one part on another (see Figure 3-7). On upward movement of the plunger, air flows into the pump through a suction valve. Downward movement of the plunger closes the suction valve and the air is forced through a discharge valve, perhaps located in the plunger itself. An automobile fuel pump is an example of a diaphragm pump.

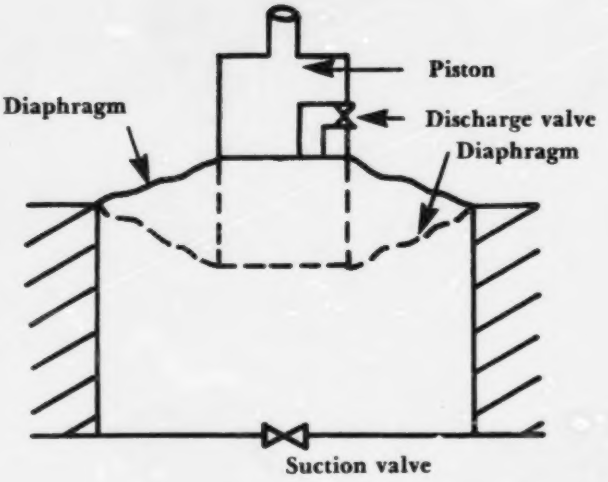

Piston
Diaphragm
Discharge valve
Diaphragm
Suction valve

Figure 3-7. Diaphragm pump.

Centrifugal Pump Operation

Centrifugal pumps (or fans) employ centrifugal force to move air. The simplest form of this type of pump consists of an impeller rotating in a volute ("snail's shell") casing (see Figure 3-8). The rotation of the impeller creates a decreasing pressure at the impeller "eye", causing air to be drawn into the pump. Air drawn into the center of the impeller is "picked up" by the vanes and accelerated to a high velocity by rotation of the impeller. It is then discharged by centrifugal force into the casing and out the discharge nozzle.

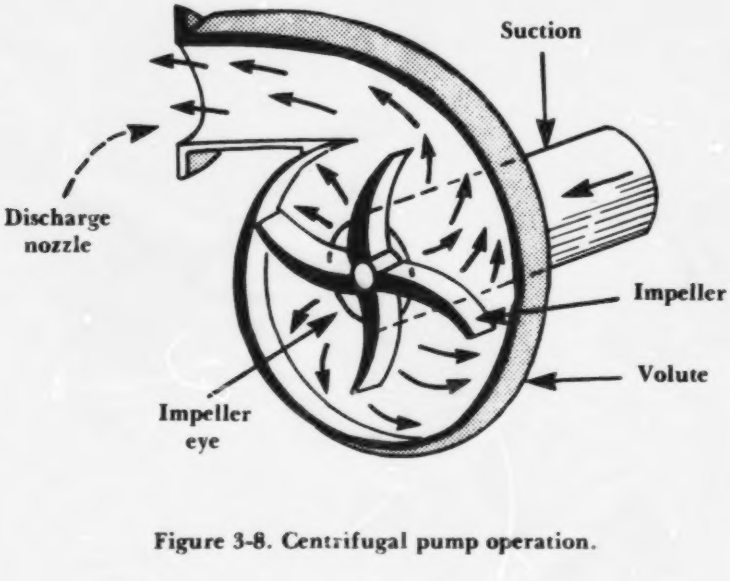

Suction
Discharge nozzle
Impeller
Volute
Impeller eye

Figure 3-8. Centrifugal pump operation.

Centrifugal pumps encountered in air sampling can be divided primarily into three categories: (a) radial flow, (b) axial flow, and (c) mixed flow. Centrifugal pumps may also be classified into single-stage or multi-stage. Single stage indicates a pump in which the total head is developed by one impeller; multistage indicates a pump having two or more impellers acting in series in one casing (13).

"Driving Forces" for Pumps

All pumps have at least one common characteristic - they have movable parts. The movement of the parts is the basis for the transfer of the particular fluid of interest. For the parts to move there must be a "driving force." Driving forces for pumps can be categorized as: (a) manual, and (b) motors.

Some air movers in the general category of pumps can be operated manually. A hand-operated hypodermic syringe (piston pump) and a tire pump using a foot pedal, are examples. The hand-operated, portable MSA Midget Impinger Sampler has seen much use. It is operated by a hand-cranked, 4-cylinder pump that draws air through a small glass nozzle at a relatively high velocity. A relatively constant flow rate can be obtained by use of this sampler. Two obvious disadvantages of manually-operated pumps is that only small sample volumes can be collected, and that sampling time is limited because of personnel requirements.

Electric motors operated by commercial power, motor-generation sets, or by batteries are all used for driving air sampling pumps. When batteries are to be used as the driving force, several factors should be considered, among which are the motor power requirements and the required length of sampling. The length of the sampling time is important in relation to the life of the battery.

In instances where constant flow is required it is important that the driving force for the pump be constant and not affected by environmental factors. If the driving force is variable, measures may have to be taken to try to regulate it. For example, a voltage regulator may be required in conjunction with an electric motor that is driving an air pump where variable voltage power sources are encountered.

Characteristic Curves

Pumps perform differently under different conditions; therefore, "characteristic curves," showing the relationships between the various conditions affecting their performance, are usually supplied by the manufacturer. The characteristic curves of most interest in air sampling are those indicating the pressure-flow relationship. See Figures 3-9 and 3-10.

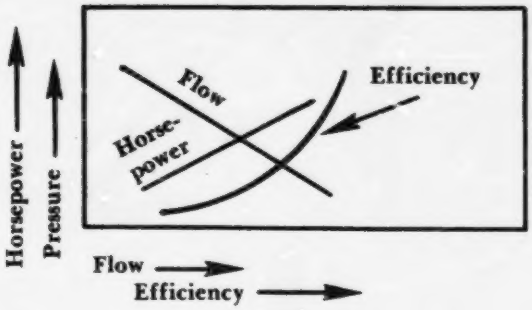


Figure 3-9. Characteristic curve for a positive displacement pump.

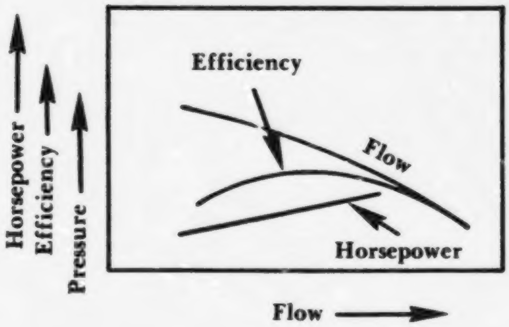


Figure 3-10. Characteristic curve for a centrifugal pump.

The quantity of flow is usually expressed in terms of a flow rate, e.g., c.f.m., ℓ.p.m., and c.f.h. The pressure represents that amount of suction that must be available to overcome the resistance of the air to movement through the sampling train. Pressure can be expressed in pounds per square inch gage (psig) or in inches of an equivalent height of a fluid. The suction pressure at which a pump is required to operate is often referred to as its head. The total head is equal to the total pressure drop between intake of the sample collection device and the pump intake. Other parameters such as efficiency, horsepower, and speed are indicated in the characteristic curves for certain pumps. Empirical equations relating various parameters are also available (8,13). It should be noted from Figures 3-9 and 3-10 that different types of pumps possess different characteristics. As flow increases for a rotary pump the efficiency increases; whereas, for a centrifugal pump the efficiency increases and then decreases as flow increases.

Selecting A Pump

It is evident that often a choice must be made between pumps. The selection may be limited to certain categories of air movers due to the sampling rate required. On the other hand, if flow rate is not critical, a wide variety of air movers may be applicable necessitating a more involved evaluation and choice. A comparison of some of the advantages and disadvantages of certain types of pumps is contained in Figure 3-11. A comparison of this type, although it is not necessarily complete in all considerations, should be of value in responsible pump selection.

Pump type	Advantages	Disadvantages
Piston pump (reciprocating)	1. Can operate at high suction pressure 2. Can be metered	1. Small capacity 2. Seal required between piston & piston chamber 3. Working parts such as check valves and piston rings may cause difficulties 4. Pulsating flow 5. Moderate maintenance
Diaphragm pump (reciprocating)	1. Wide range of capacities 2. No seal required 3. Good in continuous operation	1. Limited materials of construction 2. Operation at limited suction pressures 3. Pulsating flow 4. Periodic diaphragm replacement 5. Moderate maintenance
Centrifugal pump	1. Large range of capacities 2. No close clearance 3. Can obtain high suction heads by multistages 4. Light maintenance	1. No small capacities 2. Turbulence 3. Operational noise

Figure 3-11. Pump comparison (1, 2, 7).

There are many features of commercially available pumps that may or may not warrant consideration. Some features may have direct applicability for certain uses, others may provide flexibility making the pumps more generally useable. In this discussion only gages and continuous operation capability will be considered.

Pump Gages

Many pumps have inlet vacuum gages and/or outlet pressure gages. These gages, upon proper calibration, can be used to determine the approximate flow rate through the pump. The flow rate determination can be made by use of the pump's characteristic curve for the pressure-flow relationship (See Figure 3-12, or by direct reading if the gage is calibrated in terms of cfm on its dial).

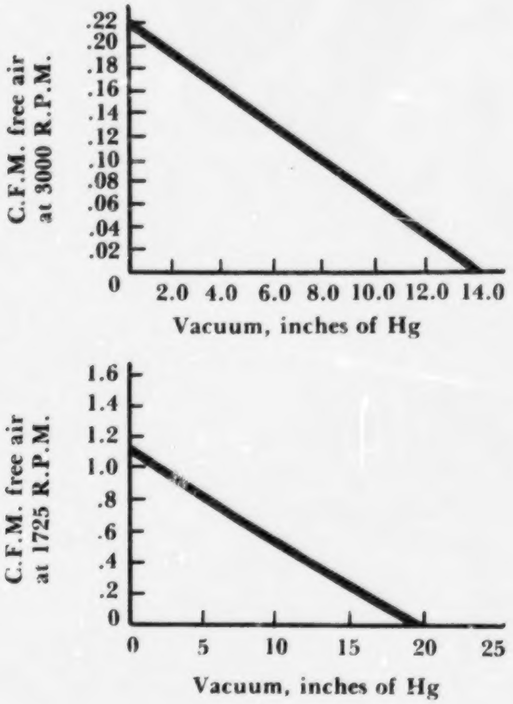


Figure 3-12. Pressure-flow relationship for metal bellows pumps for vacuum.

Continuous Operation Capability

Pumps are often required to operate continuously for long periods of time (hours to days) at high vacuum. Some pumps such as rotary or diaphragm pumps used in ambient air monitors are capable of continuous operations at high vacuum, while others would tend to "burn" themselves out. The importance of this capability would be dependent on the sampling time required.

Ejectors

Another classification of air movers is known collectively as ejectors. Ejectors are also referred to as aspirators.

Principle of Operation

As depicted in Figure 3-13, ejectors operate according to the jet principle (1). At the nozzle the pressure head of the driving force is converted into a high velocity stream. The passage of the high velocity stream through the suction chamber creates a decreased pressure (vacuum), thus drawing air into the chamber itself. The incoming air is mixed with the high velocity driving force mixture and can be ejected against moderate pressure through the diffuser.

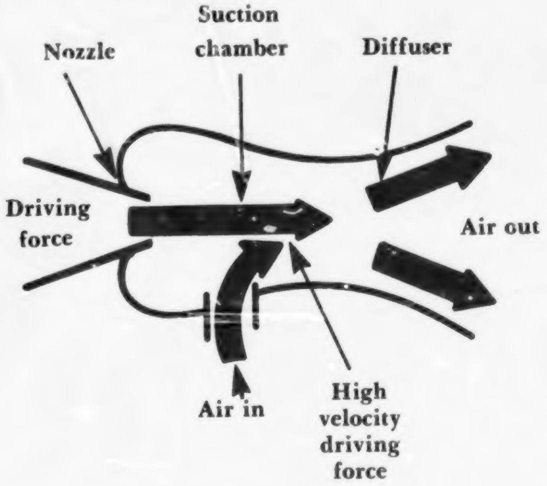


Figure 3-13. Ejector operation.

Driving Forces

The pressurized fluid that is converted into a high velocity jet stream in an ejector may be of several types.

Some examples of fluids used are water, steam, compressed air or CO_2, and other gases such as freon (1, 7).

Sampling Use of Ejectors

Using ejectors as sampler air movers is adequate for lower sampling rates. The sampling rates vary from a few liters per minute up to several cubic feet per minute. The flow rate through an ejector can be regulated to some extent by adjusting the nozzle opening. A limitation to the use of ejectors is that the pressurized driving force may have a time limit on its available effectiveness. (i.e., If a pressurized gas cylinder is used, it may last only for a limited amount of time.)

Liquid Displacement

Air movers that operate according to the principle of liquid displacement incorporate two sampling train components into one entity. In this case the liquid displacement unit serves as the sample collection device and the air mover together or may provide the air moving capability for a second device which may act as the sample collection device.

Principle of Operation

Gravity flow of liquid from a container creates a vacuum within the container; thus drawing air into the container to fill the displaced volume (see Figure 3-14).

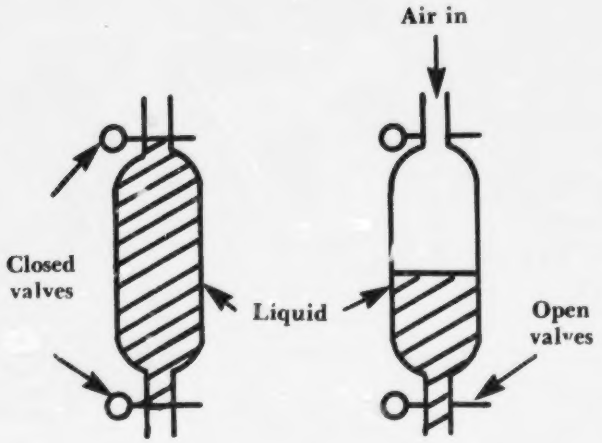


Figure 3-14. Liquid displacement.

Sampling by Use of Liquid Displacement

Liquid displacement is usually used only for grab sampling. The sample volume capacity is limited to the size of the liquid container. Some examples of liquids used are water, mercury (Hg), and organic solvents.

Evacuated Flasks

Air moving by use of evacuated flasks is another example of having the sample collection device and the air mover combined into one unit.

Principle of Operation

A flask is evacuated by a vacuum pump to a very low pressure that must be determined. The flask is sealed and transported to the sampling location. When a valve is opened on the flask, the surrounding air moves into the flask because of the pressure differential. On closing the valve, the sample is confined for subsequent analysis.

Sampling by Use of Evacuated Flasks

Evacuated flasks are usually used only for grab sampling; consequently, only relatively small sample volumes can be collected. Careful consideration should also be given to the possibility of flask "implosion" when glass containers are used, and appropriate protective means should be undertaken.

Flow Rate Control

Control by Diversion

The principle of flow diversion is simply that the air moved by the air mover is not all passed through the sample collection device. As depicted in Figure 3-15, a "bleed" valve control in the sampling train allows the variation of the actual flow through the sample collection device. The position of the flow measuring device is such that it measures only the flow passing through the sample collection device.

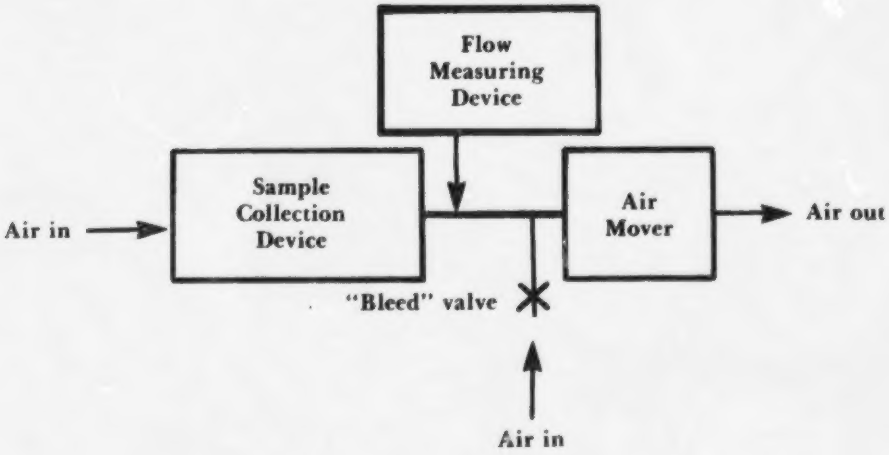


Figure 3-15. Flow rate control by diversion.

Resistance Control

In most air moving devices the flow rate decreases as the resistance it must overcome increases. Examples of this are depicted in Figures 3-9 and 3-10, which show sample characteristic curves for several pumps. The flow rate of the air mover can, therefore, be regulated by controlling the resistance it must overcome. A common method of control is to partially close a valve in the intake line, thus creating a greater resistance. Reproducible flow control can be accomplished by using needle valves with resettable marking.

Driving Force Control

It may be possible to control the air mover driving force, thereby controlling the rate of air flow. Adjustment of the nozzle opening on an ejector can be considered as a driving force control, because it affects the velocity of pressurized gas stream. The velocity of the gas stream, in turn, affects the suction pressure.

Another example of driving force control is electric motor speed regulation. This can be accomplished on some pump motors by use of a variable transformer, which controls the amount of power sent to the motor. These variable transformers are known by several names, such as variacs and powerstats.

Flow Rate for Sampling

After a particular flow rate has been selected for sampling, and after it has been set for the sampling train, it is usually necessary to maintain the flow at exactly that rate (14).

Need for Control

A variation of the desired flow rate can be caused by a variation in the air mover driving force or a variation in the resistance to air flow. The resistance to air flow is equivalent to the head the pump must overcome (suction head). Some sampling conditions affecting flow variation have been mentioned above. Flow variation during sampling may affect more than the determination of the volume of air sampled; it may also affect the performance of the sample collection device. For example, the absorption rate of a bubbler may be altered by a variation of the flow rate throught it.

Control Mechanisms

Many flowrate control mechanisms operate by keeping the effective resistance that the pump must overcome at a constant value (7, 10, 11). In other words, as depicted in Figure 3-16, the pressure drop (Δp) from the environment being sampled to the pump intake is held constant.

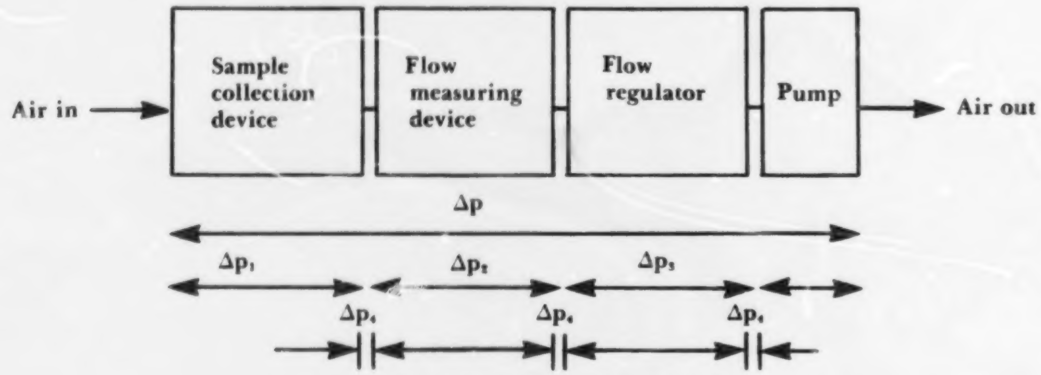


Figure 3-16. Flow rate control mechanism.

Sources of pressure drop in a system of this type include:

- the pressure drop across the sample collection device (Δp_1),
- the pressure drop across the flow measuring device (Δp_2),
- the pressure drop across the flow regulator (Δp_3),
- the pressure drop due to friction in connecting lines (Δp_4).

Friction losses and flow measuring losses are usually considered as being constant.

The resulting relationship can be shown in Equations 3-1, 3-2, 3-3, 3-4.

(Eq. 3-1) $$\Delta p = \Delta p_1 + \Delta p_2 + \Delta p_3 + \Sigma \Delta p_4$$

(Eq. 3-2) $$\Delta p_2 + \Sigma \Delta p_4 = \text{constant}$$

(Eq. 3-3) $$\Delta p - \Delta p_2 - \Sigma \Delta p_4 = \Delta p \text{ adjusted}$$

(Eq. 3-4) $$\Delta p \text{ adjusted} = \Delta p_1 + \Delta p_3$$

Initially in the sample collection, the sample collection device resistance (Δp_1) is low; therefore, the regulator would have to offer a higher resistance (Δp_3). As sampling proceeds, the sample collector resistance (Δp_1) increases; thus automatically lowering the flow regulator resistance (Δp_3) and keeping Δp_{adj} at a constant value. The regulator resistance control may be actuated by several mechanisms, usually a pressure drop directly related to time rate.

Another type of control mechanism accomplishes control by varying the pump motor speed. As the pressure drop across the sample collection device increases, a switching arrangement increases the pump motor speed – thus drawing a constant air flow.

Summary

The air mover in a sampling train is certainly an important component. There are many factors for consideration involved in the selection of an air mover. Air movers can be classified according to their principle of operation: pumps, ejectors, liquid displacement, and evacuated flasks being some of the categories. There also may be further subdivisions of the general categories of air movers. In many instances the ability to change the flow rate of the air mover and then to keep it constant at that rate are important.

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Air Measuring Instruments

Introduction

The accuracy and precision of a given method for the determination of the concentration of an air pollutant is based on two factors:

- the accuracy and precision of the sampling method;
- the accuracy and precision of the analytical method.

Examine the following term:

$$\frac{\mu g}{M^3} \left(\frac{\textit{Mass of Pollutant}}{\textit{Volume of air sampled}}\right)$$

You can see that the "μg" (***mass of pollutant***) term is a result of the analytical process, while the "M^3" (***volume of air sampled***) term is a result of the sampling process. Not only is the mass of pollutant important in the final calculation of $\mu g/M^3$, but the volume of air sampled is also important. We will concentrate in this section on the measurement of the volume of air sampled.

The accuracy and precision of the sampling method depends upon these factors:

- the environmental conditions during sampling,
- the collection efficiency of the sampling method,
- the accuracy and precision of the flow rate measurement, and
- any interferences.

The determination of the volume of air sampled, V, generally involves a measurement of flow rate, Q, and sampling time, t.

(Eq. 3-5) $$V = Q \times t$$

The flow rate during atmospheric sampling can be measured by a variety of air measuring devices. These devices and their calibrations will be discussed in this chapter.

Types of Air Measuring Devices

Air measuring devices can be broadly classified into three categories:

- volume meters,
- rate meters,
- velocity meters.

Volume meters measure the total volume, V, of gas passed through the meter over some specified time period. If the time period, t, is measured with a timing device, flow rate can be calculated by:

$$Q = \frac{V}{t}$$

Rate Meters measure the time rate of flow through them. Flow rate is measured through some property of the gas.

Velocity meters measure the linear velocity, $\bar{u}$, of a gas in a duct. Volumetric flow rate can then be calculated by measuring the cross-sectional area, A, of the duct through which the gas is flowing, by:

$$Q = A \times \bar{u}$$

Calibration

Air that is to be sampled often is moved at a known rate over a known time period. The determinative process used to establish this known flow rate and known time period is a form of calibration. Remember that it has been said before that $V = Q \times t$, or that volume sampled, V, is the product of flow rate, Q, and time t. The calibration process applied to *both* the flow rate and time allows the accurate determination of volume.

The frequency with which calibration occurs depends upon a number of conditions. Some of these are:

- instrument use—
  what are the conditions under which the instrument is used?
- instrument users—
  how many different people use the instrument? what are the qualifications of the people?
- instrument characteristics—
  how often does the instrument require calibration under controlled laboratory conditions? how sensitive is the instrument?

The basic equipment required for calibrating air flow measuring instruments include a standard meter, an air mover, and often a source of constant power.

Standard meters are of three types:

- primary standards
- intermediate standards
- secondary standards.

Primary standard meters are those whose volumes can be determined by measurement of internal physical dimensions alone. The measured internal dimensions are regular, and accuracies better than ±0.30% can be achieved. *Intermediate standards* are those standards that cannot easily be calibrated by measuring physical dimensions, but accuracies of ±1–2% can be achieved. Intermediate standards are calibrated against primary standards. *Secondary standards* are those calibrated against primary or intermediate standards under known conditions of gas type, temperature, and pressure. Accuracies less than 5% are achievable.

Volume Meters

Volume meters measure the volume of gas passing through the meter. When coupled with a timing device (like a calibrated stopwatch) flow rate (volume/time) can be calculated. There are seven volume meters that are in common use in air sampling and analysis.

The Spirometer (or "Bell Prover")—Primary Standard

The spirometer consists of a cylinder of known volume, closed at one end, with the open end submerged in a circular tank of fluid (Figure 3-17). The cylinder can be opened or closed to the atmosphere by a valve. As the cylinder is lowered into the water, the water displaces the air and causes it to be discharged from the cylinder; the rate of discharge can be regulated.

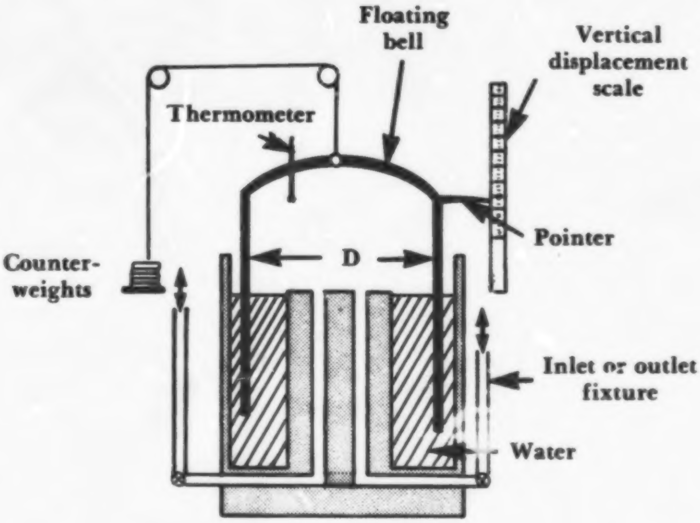

Floating bell
Vertical displacement scale
Thermometer
Pointer
Counter-weights
D
Inlet or outlet fixture
Water

Figure 3-17. Spirometer.

The volume of the cylinder is determined from its dimensions. A counter weight and cycloid counterpoise allow pressure differentials across the spirometer as low as 0.02 inches of water (Figure 3-18).

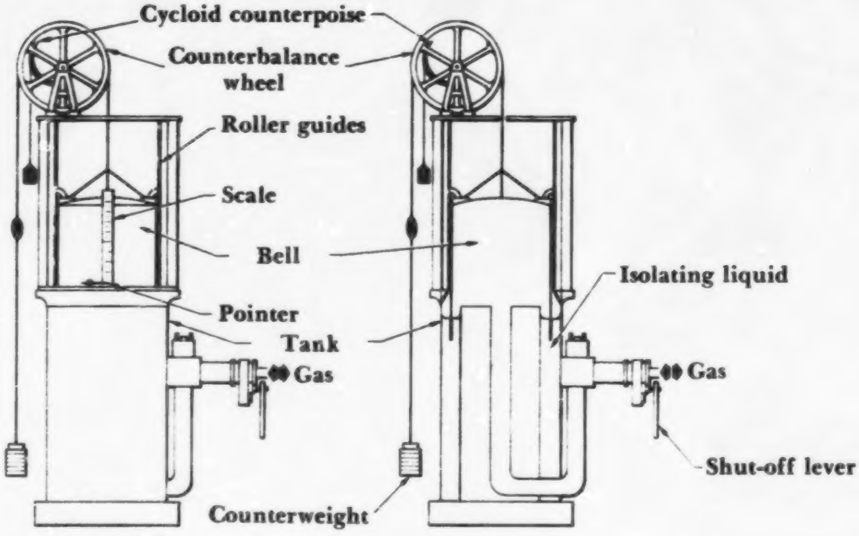

Cycloid counterpoise
Counterbalance wheel
Roller guides
Scale
Bell
Isolating liquid
Pointer
Tank
Gas
Gas
Shut-off lever
Counterweight

Figure 3-18. Orthographic and cross-sectional views of a 5-ft³ spirometer. (5)

The volume of air passed through a spirometer is given by the following formula:

(Eq. 3-6)

$$V = \frac{\pi d^2 h}{4}$$

Where:

V = *volume of air passed through spirometer*
π = *a constant* = 3.14
d = *diameter of bell*
h = *vertical displacement of bell*

The fluid in the spirometer should be at the same temperature as the room. This is to ensure that the fluid and the air will be in thermal equilibrium and thereby minimize spirometer fluid evaporating into the air. This thermal equilibrium also simplifies volume corrections since temperature is constant during the calibration procedure. This is true for water, but some spirometers use oil. The real importance of thermal equilibrium is that the air displaced from the bell must be at the same temperature as the room for volume calculations. The pressure inside the bell is also brought into equilibrium with room conditions.

Once the volume of air is determined using room conditions, a conversion to standard conditions must be made to determine the true volume of air that has passed through the spirometer. This conversion to standard conditions is made using the following formula (see Equation 2-7):

$$V_2 = V_1 \left(\frac{P_1}{760 \text{ mm Hg}}\right)\left(\frac{298\,°\text{K}}{T_1}\right)$$

The spirometer is usually calibrated by the manufacturer against an NBS "cubic-foot" bottle. If an owner suspects that his spirometer is in error he can check the calibration with an NBS certified "cubic-foot" bottle or by a "strapping" procedure.

The "strapping" procedure involves the measurement of the dimensions of the bell with a steel tape and subsequent calculation of the volume. Experienced personnel routinely obtain accuracies of ±0.2%, when calibrating a spirometer by the "strapping" procedure. Nelson gives a very detailed procedure for performing the "strapping" procedure (5). Manufacturers of spirometers include example calculations in the literature accompanying their instruments.

Flow rates can be measured by timing the volume of air passing to or from the spirometer and determining the rate of flow. The spirometer is simple, inexpensive, dependable and is used almost solely as a primary standard for calibration of other types of flow and volume measuring devices. Because the spirometer can be produced in large sizes it has typically been used to calibrate roots meters, which are positive displacement meters.

Displacement Bottle—Primary Standard

The displacement bottle consists of a bottle filled with water (or some other liquid) and a tube through which air can enter the bottle (Figure 3-19). As the liquid in the bottle is drained or siphoned out, air is drawn in, to take the place of the volume of liquid lost. The volume of gas sampled is equal to the volume of liquid displaced. The fluid in the displacement bottle should be in thermal equilibrium with the room temperature. This equilibrium will ensure no liquid evaporation from the bottle water to the air, and simplify volume corrections for *T* and *P*. The volume of displaced liquid can be measured with a graduated cylinder or Class A volumetric flask, depending on how accurately the volume needs to be measured. Accuracy can range from 1 - 5% depending on what measuring device is used.

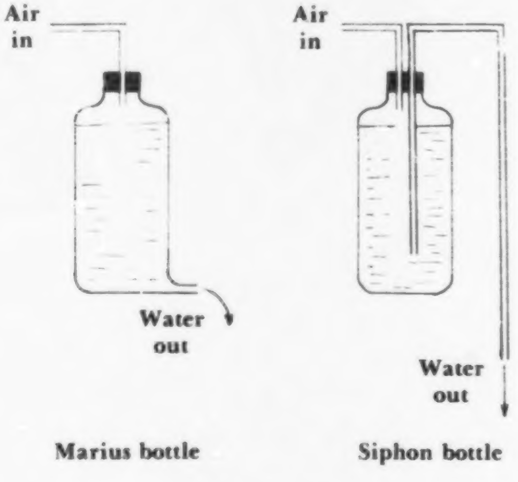


Figure 3-19. Water displacement bottles.

Again, once the volume of air has been determined at room conditions, it should be converted to the volume at standard conditions. This conversion uses the relationship previously stated in Equation 2-7.

Frictionless Pistons—Primary Standards

The soap-bubble meter and the mercury-sealed piston are two frictionless pistons that will be discussed in this section. Accurate and convenient measurement of flows between 1 and 1000 ml/min can be made with a soap bubble meter. Mercury-sealed pistons are available that can accurately measure flows from 100 cm^3/min to 24,000 cm^3/min.

Soap-Bubble Meter

A bubble meter consists simply of a cylindrical glass tube with graduated markings, usually in milliliters. Inverted burets are often used as soap-bubble meters (Figure 3-20); however, burets cannot be used with anything other than a vacuum source. Simple bubble meters (Figure 3-21) can be purchased, although the basic design can be made conveniently by a competent glass blower.

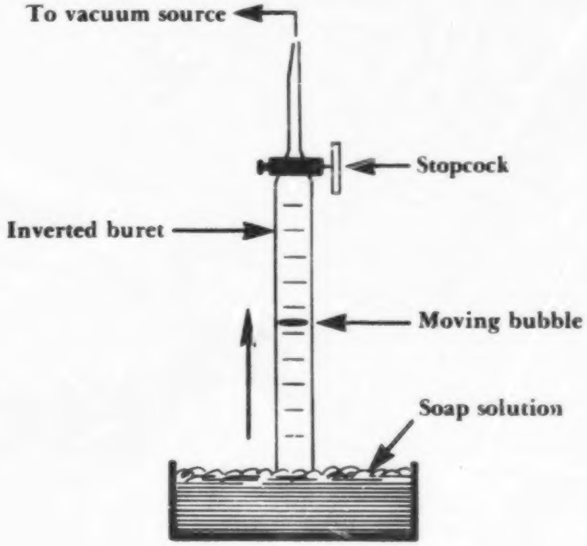


Figure 3-20. Soap-bubble meter.

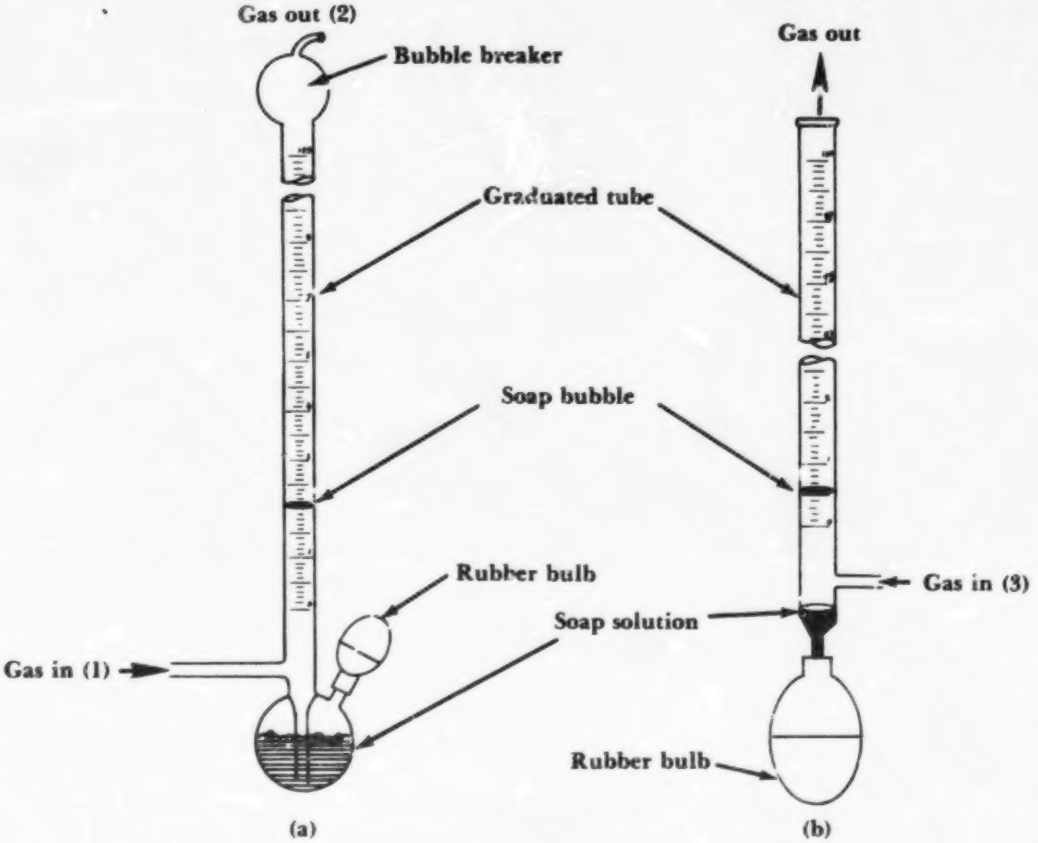


Figure 3-21. Soap-bubble meters (a) with bubble breaker and capability of handling vacuum at (2) or pressure at (1); (b) one capable of handling only pressure at (3).

The soap-bubble meter is one of the simplest of primary standards. The inside walls of the tube are wetted with a soap solution. A bubble is formed by touching the tip of the buret to the soap solution, as in Figure 3-20, or by squeezing the rubber bulb until the soap solution is raised above the gas inlet (Figure 3-21).

Either a vacuum at the top or slight positive pressure at the bottom of the tube moves the bubble (a frictionless piston) up the tube. By timing this movement and noting the volume traversed by the bubble, over the measured time span, volumetric flow rate can be calculated.

The volume measured by a soap-bubble meter must be corrected for two conditions. First, if the room temperature and pressure are different from standard atmospheric conditions the volume must be corrected by the relationship previously stated (see Equation 2-7):

(Eq. 3-7)

$$V_2 = V_1 \left(\frac{P_1}{760 \text{ mm Hg}}\right)\left(\frac{298\,°\text{K}}{T_1}\right)$$

Secondly, the measured volume can be slightly larger than the actual volume because water from the bubble evaporates into the gas behind the bubble. If the gas behind the bubble has a relative humidity greater than 50%, the error is small. If the gas is dry, the error can be large and must be corrected by the following formula:

(Eq. 3-8)

$$V_c = V_{meas}\left(\frac{P_b - P_w}{P_b}\right)$$

Where:

V_c = *corrected volume*
V_{meas} = *measured volume*
P_b = *atmospheric pressure* (mm Hg)
P_w = *vapor pressure of water at the room temperature* (mm Hg)

Note that P_b and P_w must have the same units.

Vapor pressure tables for water can be found in almost any chemistry handbook.

Soap-bubble meters can be calibrated by measuring the dimensions of the tube; however, poor control on glass dimensions in manufacturing make this inaccurate. The bubble meter is usually calibrated by filling the tube with a liquid (water or mercury for example), draining the liquid from the top graduation to the bottom graduation. The volume or weight of the collected liquid can be measured. With proper corrections for temperature this calibration is accurate. The soap-bubble meter should only be used to measure volumes between graduations that have been calibrated.

The bubble meter is used almost exclusively in laboratory situations for calibration of other air measuring instruments. In average laboratory conditions the soap-bubble meter is accurate to about ±1% depending on how accurately it is calibrated. Accuracy decreases for flows below 1 ml/min and above 1 ℓ/min mainly because of gas permeation through the bubble. A detailed description of the calibration and use of bubble meters has been published by Levy (6). Increased accuracies have been reported for bubble meters fitted with automatic sensing devices that start and stop a timer (7).

Mercury-Sealed Piston

If a bubble meter is unsuitable, an electronically actuated mercury-sealed piston may meet the need. Although the mercury-sealed piston is expensive, its accuracy (±0.2% for time intervals greater than 30 seconds) and simple operation make it an extremely useful tool.

The mercury-sealed piston consists of a precision-bored, borosilicate glass cylinder with a close fitting polyvinyl chloride piston (Figure 3-22). The piston and cylinder wall are sealed with a ring of mercury that stays in place because of its high viscosity and the closeness of the fit between the cylinder and piston. Gas entering the solenoid valve is vented until the measurement cycle is actuated. When the measurement cycle is started the solenoid valve closes the vent, allowing gas to enter the cylinder.

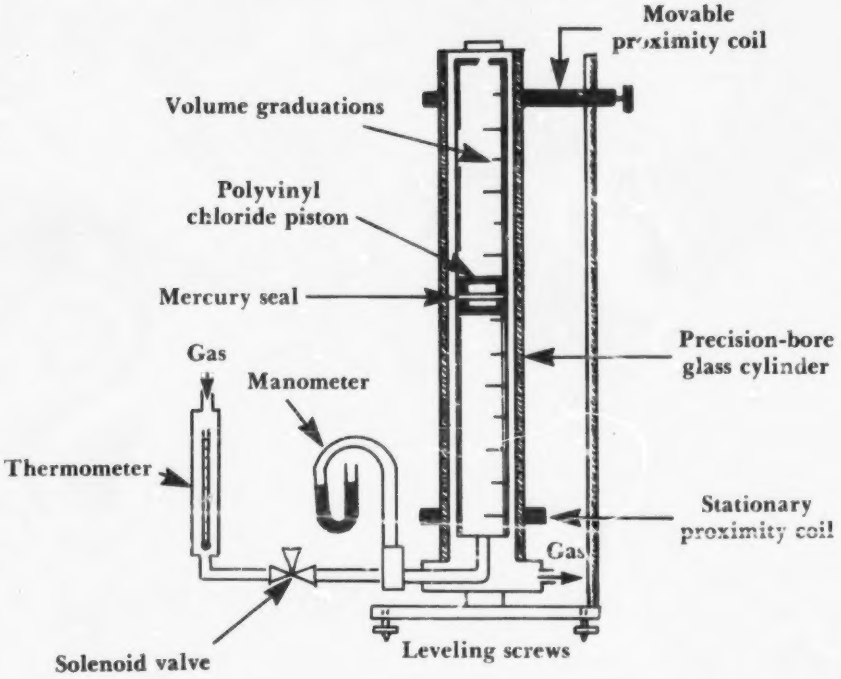

Movable proximity coil
Volume graduations
Polyvinyl chloride piston
Mercury seal
Precision-bore glass cylinder
Gas
Manometer
Thermometer
Stationary proximity coil
Gas
Solenoid valve
Leveling screws

Figure 3-22. Mercury-sealed piston volume meter.

A timer is started and stopped as the mercury seal passes the lower and upper proximity coils (metal detectors). The volume displaced can be set by adjusting the upper proximity coil. The volume is corrected to standard conditions using the pressure drop across the piston (usually <3 inches of water). The measured time and the corrected volume can be used to calculate volumetric flow. The system shown in Figure 3-23 has a reported accuracy of ±0.2%.

Calibration of the mercury-sealed piston volume meter is usually performed by the manufacturer. The borosilicate glass cylinder is bored to a precise diameter. The inside diameter is air gaged at least every inch to check for consistency. Before the instrument is sent out it is compared to a standard-mercury-sealed piston volume meter that is traceable to NBS. If a multi-cylinder unit is purchased then the cylinders must be aligned. One cylinder is chosen to be correct and all others are aligned with the set screw located on top of the piston (Figure 3-24), which changes the displaced volume slightly.

The mercury-seal can be broken by erratic movement of the instrument. For this reason the mercury-sealed piston instrument is used as a primary standard in laboratory settings. Mercury-sealed piston volume meters are available for accurate flow measurement over a wide range (100 cm^3/min to 24,000 cm^3/min).

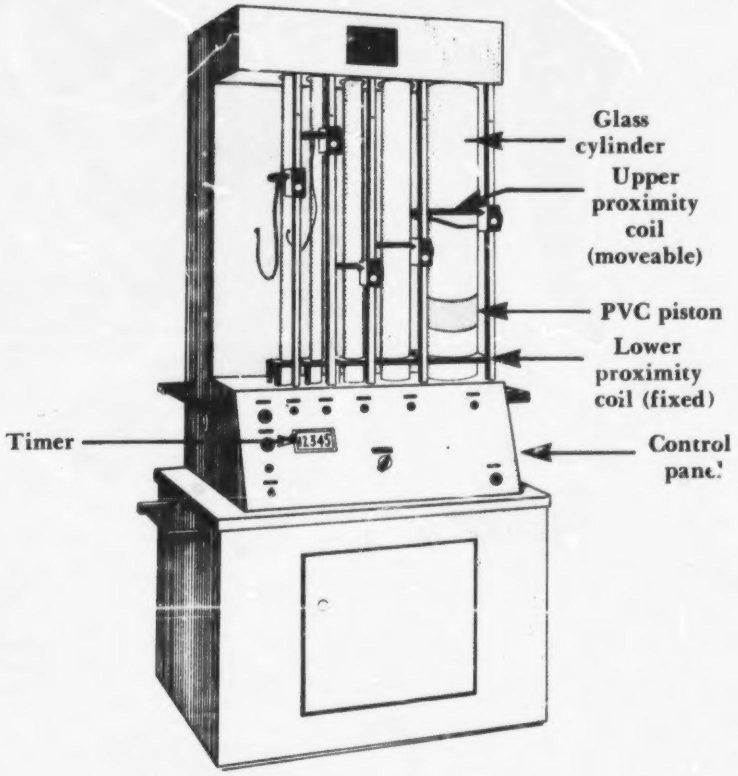

Glass cylinder
Upper proximity coil (moveable)
PVC piston
Lower proximity coil (fixed)
Timer
12345
Control panel

Figure 3-23. Calibrator console, front view (Brooks model 1051). (Courtesy Brooks Instrument Division, Emerson Electric Co.)

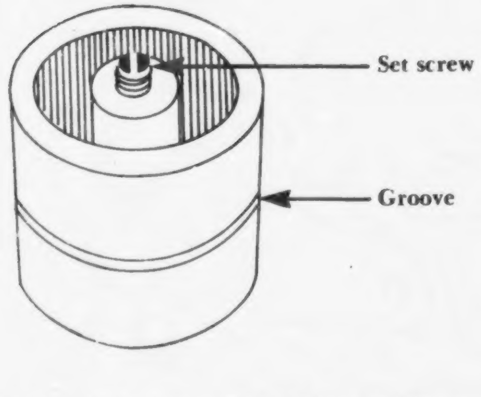

Set screw
Groove

Figure 3-24. PVC piston for mercury-sealed piston volume meter.

Wet Test Meter—Intermediate Standard

The wet test meter consists of a series of inverted buckets or traps mounted radially around a shaft and partially immersed in water (Figure 3-25c). The location of the entry and exit gas ports is such that the entering gas fills a bucket, displacing the water and causing the shaft to rotate due to the lifting action of the budget full of air. The entrapped air is released at the upper portion of the rotation and the bucket again fills with water. In turning, the drum rotates index pointers that register the volume of gas passed through the meter (Figure 3-25b).

After the meter is leveled, the proper water level is achieved by using the filling funnel, fill cock, and drain cock (Figure 3-25a) to bring the meniscus of the water in touch with the tip of the calibration index point. The calibration gas should be passed through the meter for one hour to saturate the water with the gas. The water in the meter should be at the same temperature as the surrounding atmosphere. If any water is added, sufficient time must be allowed for complete equilibration.

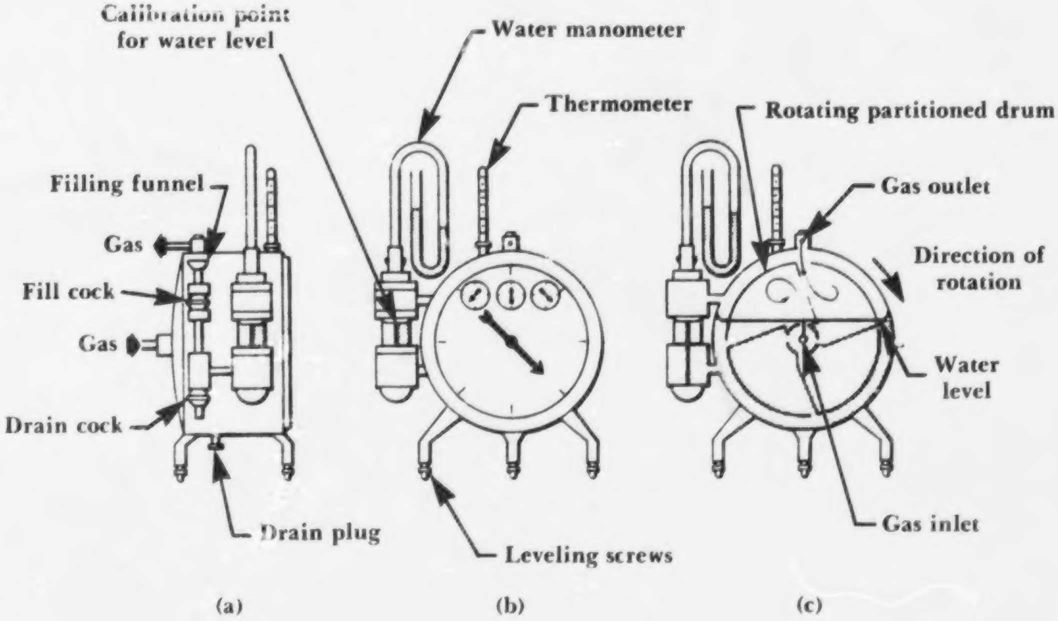

Calibration point for water level
Water manometer
Thermometer
Rotating partitioned drum
Filling funnel
Gas
Fill cock
Gas
Drain cock
Drain plug
Leveling screws
Gas outlet
Direction of rotation
Water level
Gas inlet
(a)
(b)
(c)

Figure 3-25. Wet test meter.

Once the water level is set and the meter is equilibrated, the wet test meter is ready for calibration (or use if it is already calibrated.) An accurate calibration of a wet test meter can be done with a spirometer (Figure 3-26).

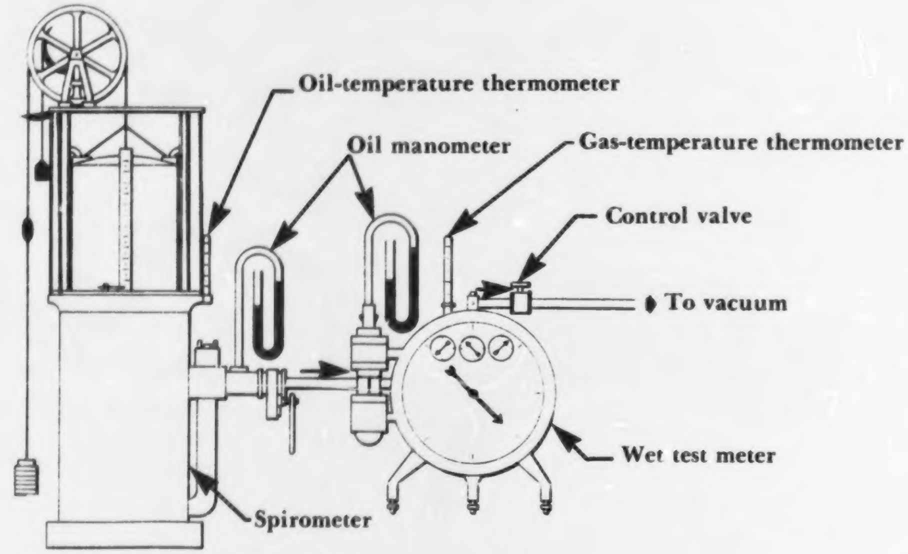

Oil-temperature thermometer
Oil manometer
Gas-temperature thermometer
Control valve
To vacuum
Wet test meter
Spirometer

Figure 3-26. Setup for calibrating a wet test meter against a spirometer. (Ref. 5)

The wet test meter can also be calibrated against a mercury-sealed piston as shown in Figure 3-27.

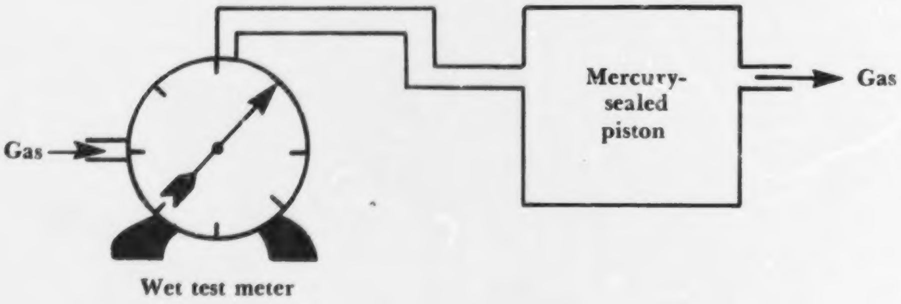

Gas
Mercury-sealed piston
Gas
Wet test meter

Figure 3-27. Calibration of wet test meter (WTM) against a mercury-sealed piston.

Enough gas is drawn through either system (Figure 3-26 or 3-27) to turn the wet test meter at least three revolutions and to significantly move the spirometer drum or piston. This measurement is made several times. Atmospheric pressure and temperature, and the temperature and pressure differential for both the wet test meter and calibrating device, are needed to correct the volume to standard conditions (taking pressure differentials into consideration). Since both the calibration device and the wet test meter are measuring gas saturated with water vapor in Figures 3-26 and 3-27, there is no need to correct for water vapor effects.

If a wet test meter is used to measure a dry gas stream, a significant error is introduced if the measured volume is not corrected to dry conditions. This correction is the same as for the soap-bubble meter correction:

$$V_c = V_{meas}\left(\frac{p_b - P_w}{p_b}\right)$$

A simple calibration check can be performed using a displacement bottle as shown in Figure 3-28. After all the water is thermally equilibrated, the wet test meter is properly set up, and the drain tube of the displacement bottle is filled, the pinch clamp is opened allowing 2 liters of water to drain into a 2-liter class A volumetric flask. The corresponding wet test meter readings are taken. This is repeated several times (usually 4).

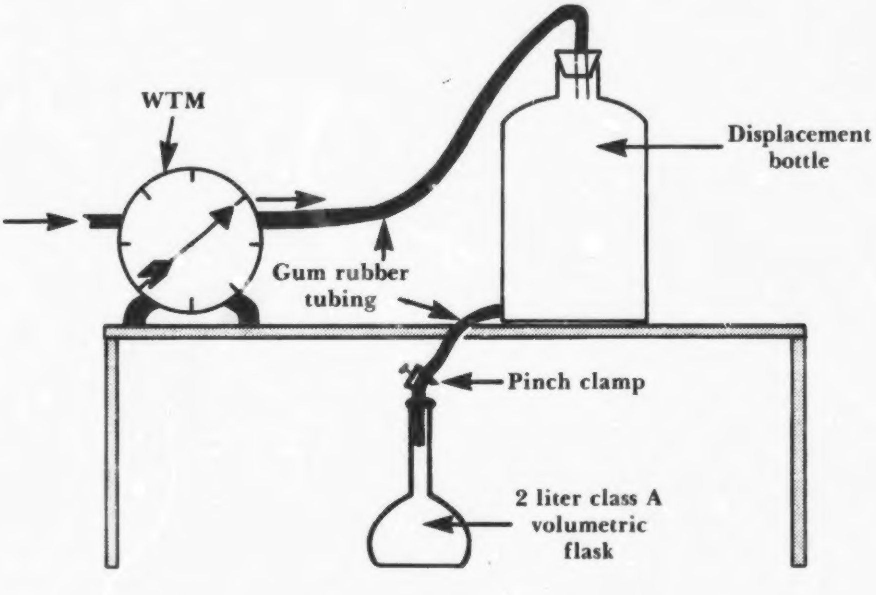


Figure 3-28. Calibration of wet test meter with displacement bottle.

The calibration data can be used to:

Option 1: Draw a multipoint calibration curve for flow for Figures 3-26 and 3-27 set ups.

Option 2: Adjust the calibration index point so that the meter volume is correct.

Option 3: Calculate a correction factor for the wet test meter.

Wet test meters should check within ±0.5% if option 2 is used.

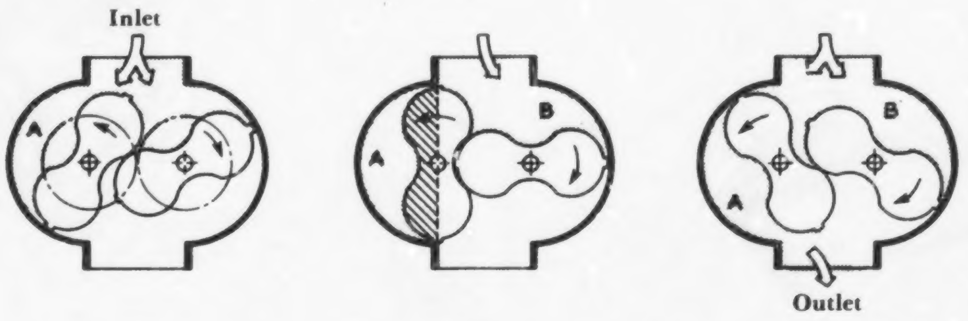
All volumes measured by a wet test meter should be corrected to standard conditions by Equation 2-7.

Wet test meters are used as transfer standards because of their high accuracy (less than ±1%). Because of their bulk, weight, and equilibration requirements they are seldom used outside a laboratory setting. Wet test meters are useful for laboratories that need an accurate standard yet do not have the funds or space for a spirometer or mercury-sealed piston. Wet test meters can be used to measure flow rates up to 3 rev/min, at which point the meter begins to act as a limiting orifice and obstructs the flow. Typical ranges of wet test meters are 1, 3, and 10 ℓ/rev.

Roots Meter—Intermediate Standard

The Roots meter is a positive displacement rotary type meter for measuring volume flow. It is suitable for handling most types of clean, common gases. It is not suitable for handling liquids, and its operation can be impeded by excessive particulates carried in the gas stream.

Roots meters consist basically of two oppositely rotating impellers of two-lobe or "Figure 8" contour, operating within a rigid casing (Figure 3-29). The casing is arranged with inlet and outlet gas connections on opposite sides. Impeller contours are mathematically developed and accurately produced, and are of such form that a continuous seal without contact can be maintained between the impellers at all positions during rotation. To accomplish this, the correct relative impeller positions are established and maintained by precision-grade timing gears. Similar seals exist between the tips of the impeller lobes and the two semicircular parts of the meter casing. As a result of this design, the gas inlet side of the meter is always effectively isolated from the gas at the outlet side of the impellers. Consequently, the impellers can be caused to rotate by a very small pressure drop across the meter.



Position 1 **Position 2** **Position 3**

Figure 3-29. Principle of gas flow through the Roots meter.

The rotation of the impellers is in the direction indicated in Figure 3-29, and as each impeller reaches a vertical position (twice in each revolution) it traps a known specific volume of gas between itself and the adjacent semicircular portion of the meter casing at A and B (Figure 3-29, Position 2). Thus, in one complete revolution the meter will measure and pass four similar gas volumes, and this total volume is the displacement of the meter per revolution.

The displacement of volume of the roots meter is precisely determined by the manufacturer, both by calculation and by testing it using a known volume of air or other gas. Roots meters are usually calibrated against large spirometers prior to shipment. Users do not usually have a way to calibrate roots meters and must depend on the supplied calibration data. Volumetric accuracy of the Roots meter is permanent and nonadjustable (except for linkage adjustment), because its measuring characteristics are established by the dimensions and machined contours of nonwearing fixed and rotating parts.

The revolutions of the impellers are indexed with the meter reading calibrated in a volume unit (i.e., ft³ or m³). Units are sold that have temperature compensation devices, but corrections to standard temperature and pressure conditions are easily made with the previously mentioned formula (see Equation 2-7) (pressure drop across the roots meters should be taken into consideration):

(Eq. 3-9)

$$V_2 = V_1 \left(\frac{P_1}{760 \text{ mm Hg}}\right)\left(\frac{298\,^\circ\text{K}}{T_2}\right)$$

The symbol P_1, in this instance, is the atmospheric room pressure (P_b, in mm Hg) minus the pressure drop across the roots meter Δp, in **mm Hg**.

(Eq. 3-10)

$$P_1 = P_b - \Delta p$$

The metering unit is magnetically coupled to the impellers. The entire counting unit is enclosed in a plastic cover. The cover also holds an oil that lubricates the metering device. The proper oil level is set by the inscribed oil level lines on the ends of the plastic covers. The user of a roots meter must be careful not to severely tilt the roots meter when oil is in the plastic cover as this can force oil into the impeller casing. If the oil gets into the impeller casing, flushing with kerosene can remove the oil.

Although roots meters are widely used in industrial applications, they have been used almost exclusively as the standard for high-volume sampler flow rate in atmospheric sampling applications.

Dry Test Meter—Intermediate Standard

Dry *test* meters are an improvement over the more common dry *gas* meters (Figure 3-30). Dry *gas* meters (a secondary standard) are most commonly used in residential and industrial settings to measure gas flow (e.g., natural gas). The dry *test* meter (an intermediate standard) works on the same principle as the dry *gas* meter, (a secondary standard) but a different indexing method (read out) makes it more accurate (usually ± 1 to 2% when new). The dry *test* meter shown in Figure 3-31 shows the new readout mechanism.

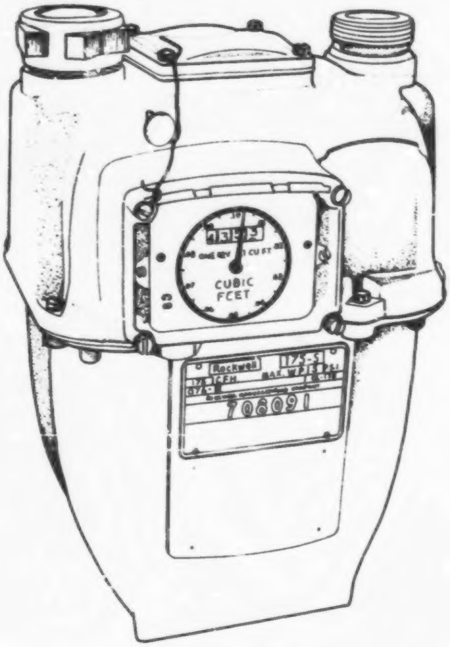
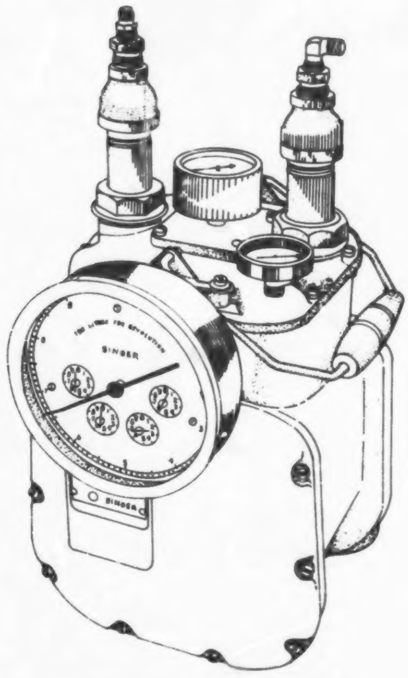

CUBIC
FEET
Rockwell
706091

Figure 3-30. Dry gas meter.


SINGER
SINGER

(Courtesy of Western
Precipitation Division,
Joy Manufacturing Company)

Figure 3-31. Dry test meter.

The interior of the dry test meter contains two or more movable partitions, or diaphragms, attached to the case by a flexible material so that each partition may have a reciprocating motion (Figure 3-32). The gas flow alternately inflates and deflates each bellows chamber, simultaneously actuating a set of slide valves that shunt the incoming flow at the end of each stroke. The inflation of the successive chambers also actuates, through a crank, a set of dials that register the volume of gas passed through the meter.

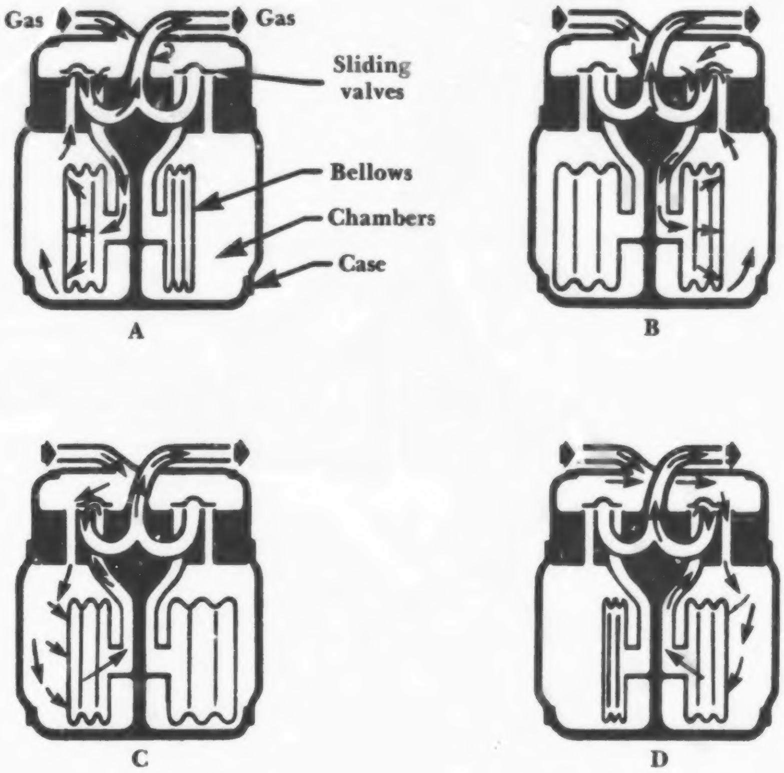


Figure 3-32. Working mechanism of dry.test meter.

The dry test meter is calibrated against a spirometer, mercury-sealed piston, or displacement bottle similar to the wet test meter. One big advantage of the dry test meter over the wet test meter is that no correction for water vapor is needed. If the dry test meter is off calibration by more than 2% it can be corrected by adjustment of the meter linkage. If linkage adjustment cannot correct the problem, then the dry test meter must be returned to the manufacturer for repairs.

Dry test meters are used in the field as well as laboratory calibrations. Since the dry test meter does not contain water, it is lighter and easier to use than the wet test meter. Also, the dry test meter is more rugged than the wet test meter. Accuracy of the dry test meter does, however, worsen with age.

Rate Meters

The most popular devices for measuring flow rate are the rate meters. Rate meters measure, indirectly, the time rate of the fluid flow through them. Their response depends on some property of the fluid related to the time rate of the flow.

Variable Pressure Meters—Head Meters

Head meters are those in which the stream of fluid creates a significant pressure difference that can be measured and correlated with the time rate of flow. The pressure difference is produced by a constriction in the stream of flow causing a local increase in velocity.

Orifice Meter—Noncritical—Secondary Standard

An orifice meter can consist of a thin plate having one circular hole coaxial with the pipe into which it is inserted (Figure 3-33). Two pressure taps, one upstream and one downstream of the orifice, serve as a means of measuring the pressure drop, which can be correlated to the time rate of flow. Watch jewels (9), small bore tubing, and specially manufactured plates or tubes with small holes have been used as orifice meters. The pressure drop across the orifice can be measured with a manometer, magnehelic, or pressure gage.

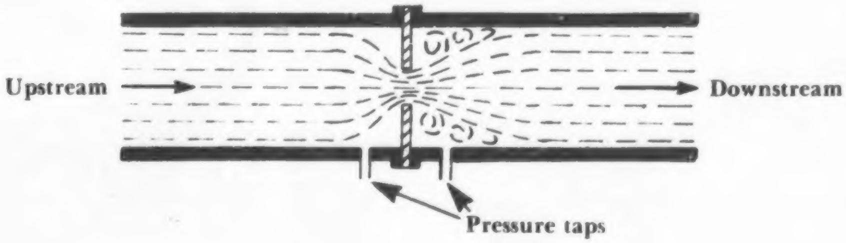


Figure 3-33. Orifice meter.

Flow rates for an orifice meter can be calculated using Poiseuille's Law; however, this is not done for practical use. Instead the orifice meter is usually calibrated with either a wet or dry test meter or a soap bubble meter. A typical calibration curve is shown in Figure 3-34.

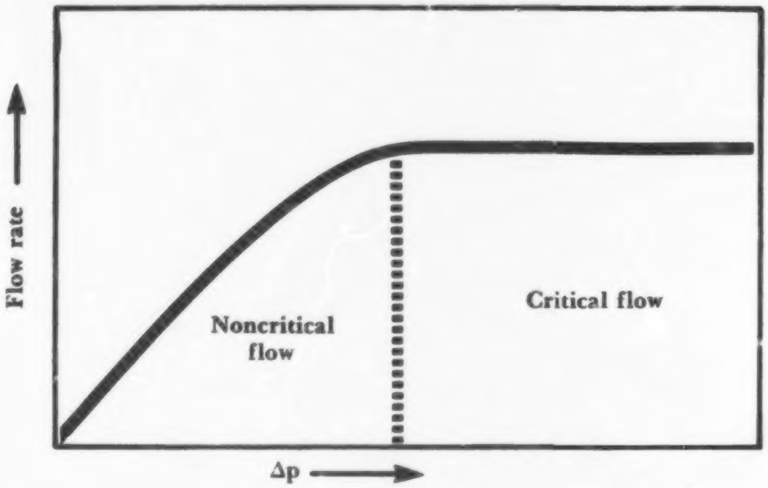


Figure 3-34. Typical orifice meter calibration curve.

Calibration curves for orifice meters are nonlinear in the upper and lower flow rate regions and are usually linear in the middle flow rate region.

Orifice meters can be made by laboratories with a minimum of equipment. They are used in many sampling trains to control the flow. Care must be exercised to avoid plugging the orifice with particles. A filter placed upstream of the orifice can eliminate this problem. Orifice meters have long been used to measure and control flows from a few ml/min to 50 ℓ/min.

Orifice Meter—Secondary Standard

If the pressure drop across the orifice (Figure 3-33) is increased until the downstream pressure is equal to approximately 0.53 times the upstream pressure (for air and some other gases), the velocity of the gas in the constriction will become acoustic or sonic. Orifices used in this manner are called critical orifices. The constant 0.53 is purely a theoretical value and may vary. Any further decrease in the downstream or increase in the upstream pressure will not affect the rate of flow. As long as the 0.53 pressure relationship exists, the flow rate remains constant for a given upstream pressure and temperature, regardless of the value of the pressure drop (Figure 3-34). The probable error of an orifice meter is in the neighborhood of 2 percent.

Only one calibration point is needed for a critical orifice. The critical flow is usually measured with a soap-bubble meter or a wet or dry test meter. Corrections for temperature and pressure differences in calibration and use are made with the following formula:

(Eq. 3-11)

$$Q_2 = Q_1 \left(\frac{P_1 \times T_2}{P_2 \times T_1} \right)^{1/2}$$

Where: Q = *flow*
P = *pressure*
T = *temperature in* °K
1 = *initial conditions*
2 = *final conditions*

The same formula can be used to correct orifice meter flows to standard conditions by substituting $P_2 = 760$ mm Hg and $T_2 = 298$ °K. Note the square root function of T and P. *Any time that rate meters are corrected for T and P, this square root function is needed.*

Critical orifices are used in the same type of situations as noncritical orifices. Care must also be taken not to plug the orifice.

Venturi Meter—Secondary Standard

The venturi meter consists of a short cylindrical inlet, an entrance cone, a short cylindrical throat, and finally a diffuser cone (Figure 3-35). Two pressure taps, one in the cylindrical inlet and one in the throat, serve to measure the pressure drop. There is no abrupt change of cross section as there is with an orifice, thus the flow is guided both upstream and downstream, eliminating turbulence and reducing energy losses. Venturi meters are, of course, more difficult to fabricate. The probable error of a venturi is 1 percent.

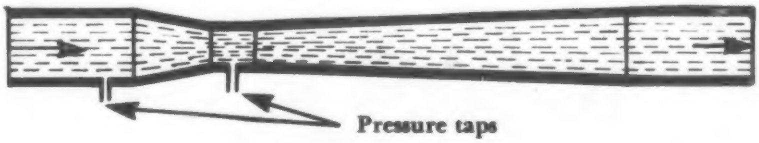


Figure 3-35. Venturi meter.

The venturi meter is calibrated in the same manner as the orifice meter. The calibration curve generated plots pressure drop across the venturi versus flow rates determined by the standard meter.

Variable Area Meters

The variable area meter differs from the fixed orifice; the pressure drop across it remains constant while the cross-sectional area of the constriction (annulus) changes with the rate of flow. A rotameter is an example of a variable area meter.

The Rotameter—Secondary Standard

The rotameter consists of a vertically graduated glass tube, slightly tapered in bore, with the diameter decreasing from top to bottom, containing a float of the appropriate material and shape (Figure 3-36). The fluid to be measured passes upward through the conical tube, which is inserted in the flow circuit.

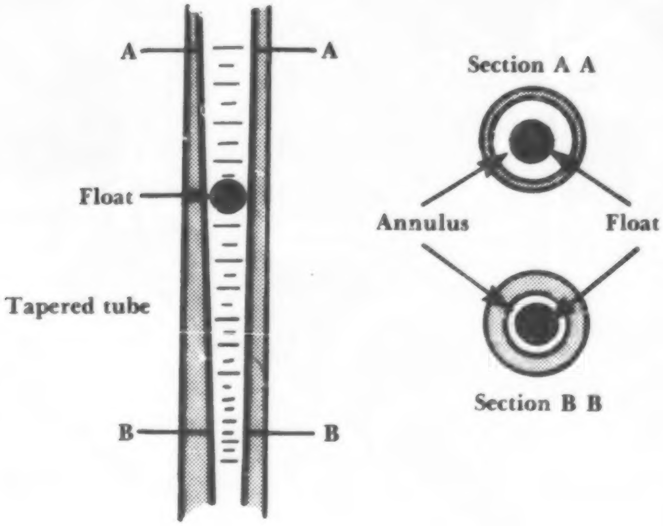


Figure 3-36. Rotameter.

A specially shaped float, with a diameter slightly greater than the minimum bore of the conical tube, is carried upward by the passage of the fluid until it reaches a position in the tube where its weight is balanced by the upward forces due to the fluid flowing past it. A variable ring or annulus is created between the outer diameter of the float and the inner wall of the tube. As the float moves upward in the tube, the area of the annulus increases. The float will continue to move upward until a pressure drop across the float, which is unique for each rotameter, is reached. This pressure drop across the float is constant regardless of the flow rate. A measure of the flow is noted by the float position on a vertical scale compared with a calibration chart.

The flow rate through a rotameter can be calculated from the tube diameters, float dimensions, float composition, and gas characteristics; this is not commonly done for calibration purposes. A detailed development of the flow equations for rotameters is contained in the appendix of this manual. Manufacturers generally provide accurate calibration curves for rotameters; it is advisable, however, to calibrate a rotameter under its operating conditions.

Most rotameters are used and calibrated at room temperature with the downstream side at atmospheric pressure. Corrections for pressure and temperature variations can be made using the previously mentioned formula:

(Eq. 3-12)

$$Q_2 = Q_1 \left(\frac{P_1 \times T_2}{P_2 \times T_1} \right)^{1/2}$$

If a gas is measured with a different density from the calibration gas the flowrate can be corrected using the following formula:

(Eq. 3-13)

$$Q_1 = Q_2 \left(\frac{\varrho_2}{\varrho_1} \right)^{1/2}$$

Where:
Q_1 = *flow rate with gas* 1
Q_2 = *flow rate with gas* 2
ϱ_2 = *density of gas* 2
ϱ_1 = *density of gas* 1

Because corrections of this type are cumbersome and add inaccuracies, rotameters are usually calibrated under normal operating conditions against a primary or intermediate standard.

Rotameters are the most widely used laboratory and field method for measuring gas or liquid flow. Their ease of use make them excellent for spot flow checks. Many atmospheric sampling instruments use rotameters to indicate the sample flow rate. With proper calibration, the rotameter's probable error is 2-5%.

Velocity Meters

Velocity meters measure the linear velocity or some property that is proportional to the velocity of a gas. Several instruments exist for measuring the velocity of a gas; we will discuss only the pitot tube and the mass flow meter. Volumetric flow information can be obtained from velocity data, if the cross-sectional area of the duct is known, using the following formula:

(Eq. 3-14)

$$Q = A\bar{v}$$

Where:
Q = *volumetric flowrate* (m^3/min)
A = *cross sectional area* (m^2)
$\bar{v}$ = *average velocity* (m/min)

Pitot Tube

The pitot tube is a simple pressure-sensing device used to measure the velocity of a fluid flowing in an open channel. The complexity of the underlying fluid flow principles involved in a pitot tube gas velocity measurement is not apparent in the simple operation of this device. The pitot tube should, however, be considered and treated as a sophisticated instrument.

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The pitot tube actually measures the velocity pressure (Δp) of a gas stream. Gas streamlines approaching a round object placed in a duct, flow around the object except at point "P_t," where the gas stagnates and the stagnation pressure (P_t) is found (Figure 3-37 and Figure 3-38a).

The static pressure in a gas stream is defined as the pressure that would be indicated by a pressure gage if it were moving along with the stream so as to be at rest or relatively "static" with respect to the fluid. The static pressure can be measured as shown in Figure 3-38b.

The difference between the stagnation pressure (P_t) and the static pressure (P_s) is the velocity pressure differential (Δp). This is shown in Figure 3-38c.

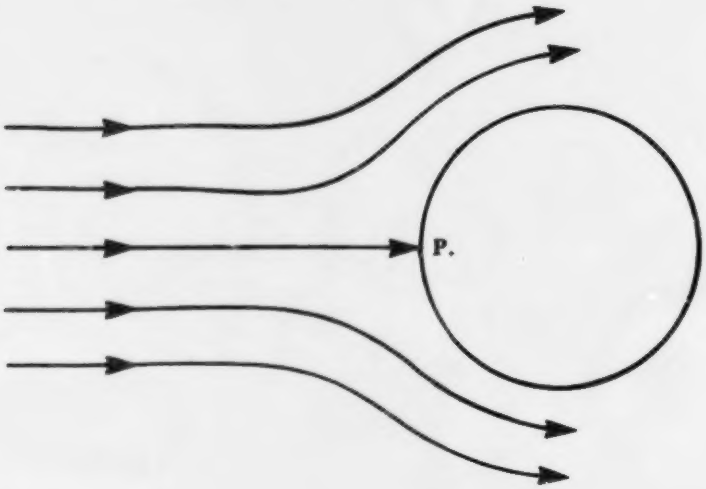
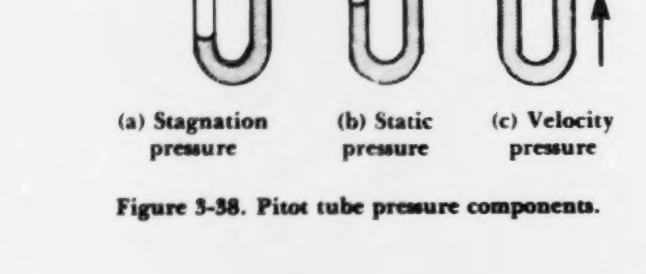


Figure 3-37. Gas stagnation against an object.



(a) Stagnation pressure **(b) Static pressure** **(c) Velocity pressure**

Figure 3-38. Pitot tube pressure components.

Bernoulli's Theorem relates pitot tube velocity pressure (Δp) to gas velocity in the following equation:

(Eq. 3-15)
$$v = K_p C_p \left(\frac{T\Delta p}{PM}\right)^{1/2}$$

Where:

v = *velocity of the gas stream, ft/sec*

T = *absolute temperature, °R (°F + 460)*

P = *absolute pressure, in. Hg*

M = *molecular weight of the gas, lb/lb-mole*

Δp = *velocity pressure, in.* H_2O

K_p = *constant:* $85.49 \sqrt{\dfrac{ft^2 \text{ in. Hg lbs/lb-mole}}{sec^2 \text{ in. } H_2O\ °R}}$ *for the above dimensions*

C_p = *pitot tube coefficient, dimensionless*

Pitot tubes are used extensively in ventilation work to measure air flow in ducts. Literature sources describe pitot tubes in detail (2, 11). The standard and S-type pitot tubes are the most commonly used.

Standard Pitot Tube—Primary Velocity Standard

The standard pitot tube (Figure 3-39) consists of two concentric tubes. The center tube measures the stagnation or impact pressure while the static pressure is measured by the holes located on the side of the outer tube. The pitot tube must be placed in the flowing air stream so that it is parallel with the streamlines. The velocity pressure differential (Δp) can be measured with a U-tube manometer, an inclined manometer, or any suitable pressure-sensing device. Only velocities greater than 2500 ft/min can be measured with a U-tube manometer, while flows as low as 600 ft/min can be measured with a carefully adjusted inclined manometer. Standard pitot tube velocity pressures are typically 0.14 inches of water at 1500 ft/min and 0.56 inches of water at 3000 ft/min.

The standard pitot tube was first calibrated against an orifice meter using Bernoulli's Theorem. Repeated calibrations proved that different standard pitot tubes have the same characteristic flow calibration. If the static pressure holes are 6 outer tube diameters from the hemispherical tip and 8 outer tube diameters from the bend (Figure 3-39), then the C_p value in the previously mentioned formula is 1.

$$v = K_p C_p \left(\frac{T\Delta p}{PM}\right)^{1/2}$$

Standard pitot tubes can be used to measure linear velocity in almost any situation except in particulate-laden gas streams. The particulates will foul the carefully machined tip and orifices. The velocity of gas streams with high particulate concentrations can be measured better with an S-type pitot tube.

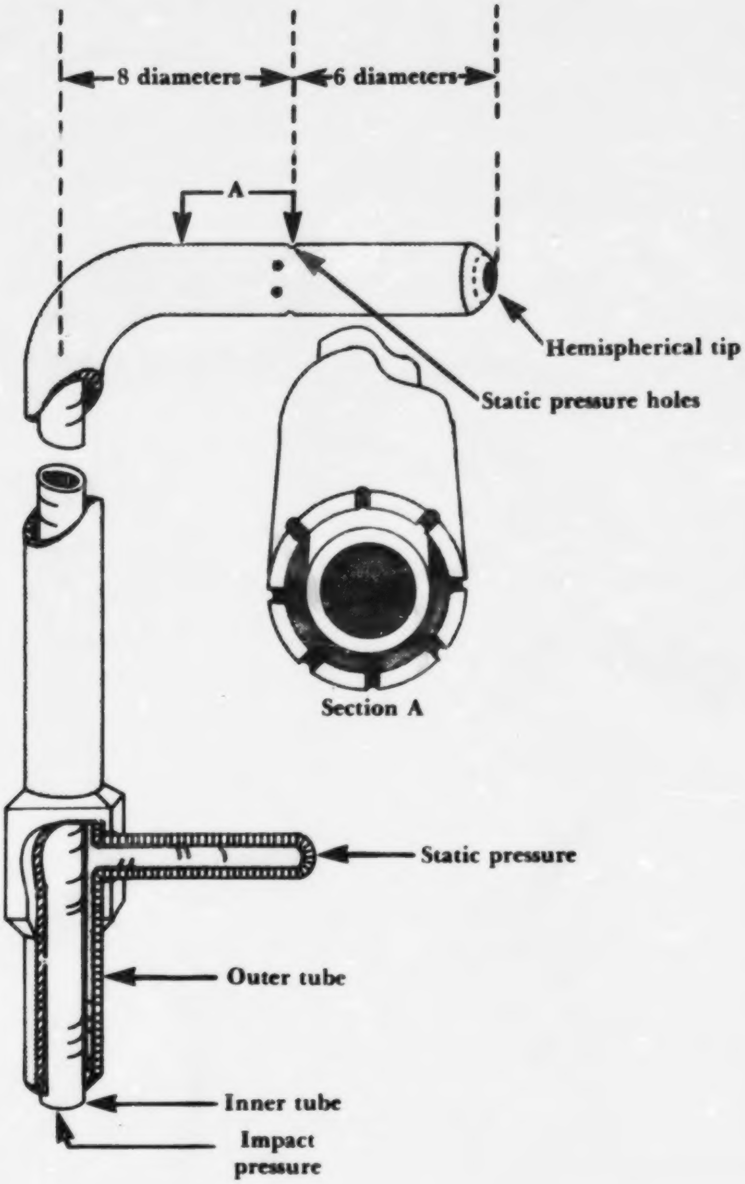

8 diameters
6 diameters
A
Hemispherical tip
Static pressure holes
Section A
Static pressure
Outer tube
Inner tube
Impact pressure

Figure 3-39. Standard pitot tube.

S-Type Pitot Tube

The S-type pitot tube consists of two identical tubes mounted back to back (Figure 3-40). The sampling end of the tubes are oval with the openings parallel to each other. In use, one oval opening should point directly upstream, the other directly downstream. The tubes should be made of stainless steel or quartz if they are used in high temperature gas streams. The alignments shown in Figure 3-40 should be checked before use or calibration as this may cause variations in the calibration coefficient (C_p).

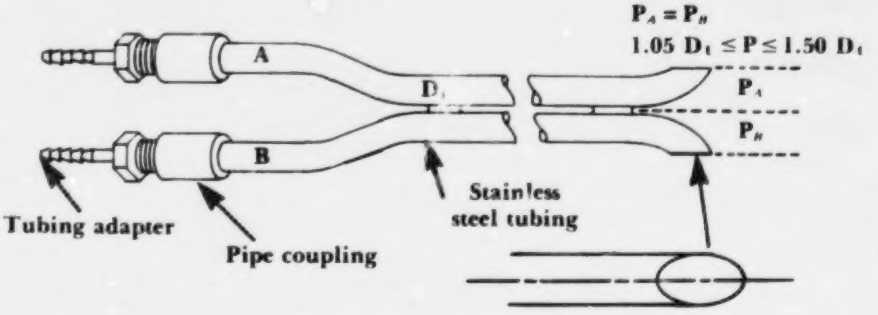


Figure 3-40. S-type pitot tube.

Calibration of the S-type pitot tube is performed by comparing it to a standard pitot tube. Both the standard and S-type pitot tubes are placed alternately into a constant air flow. Pressure readings are taken for the standard pitot tube and for leg A of the S-type tube forcing the direction of flow and leg B facing the direction of the flow (Figure 3-40). The pitot tube coefficient (C_p) is calculated using the following formula:

(Eq. 3-16)
$$C_{p(S)} = C_{p(STD)} \left(\frac{\Delta p_{STD}}{\Delta p_S} \right)^{1/2}$$

The average C_p is calculated from several readings and should have a value of approximately 0.84. The C_p for leg A and leg B should differ by less than 0.01. The C_p value can then be used to calculate velocity by the previously mentioned formula.

(Eq. 3-17)
$$v = K_p C_p \left(\frac{T \Delta p}{PM} \right)^{1/2}$$

The S-type pitot tube maintains calibration in abusive environments. The large sensing orifices minimize the chance of plugging with particulates. The S-type pitot tube also gives a high manometer reading for a given gas velocity pressure, which can be helpful at low gas velocities. These features make the S-type pitot tube the most frequently used instrument to measure stack gas velocity.

Mass Flow Meter—Secondary Velocity Standard

Mass flow meters work on the principle that when a gas passes over a heated surface, heat is transferred from this surface to the gas. The amount of current required to keep the surface at a constant temperature is a measure of the velocity of the gas. Since the amount of heat transferred depends on the mass and velocity of the gas, these meters measure mass flow rate.

Atmospheric sampling applications of the mass flow meter are usually limited to the measurement of volumetric flow. Since these devices measure mass flow directly they should be calibrated against a primary, intermediate, or secondary volumetric standard. The standard meter flow is corrected to standard conditions and compared to the mass flow rate measured. No corrections for temperature and pressure need to be made to the mass flow meter readings. Calibration must be done with the same gas as will be measured in use because different gases have different thermal properties.

Mass flow meters are most often used for flow measurement or as calibration transfer devices in the field and laboratory. Their insensitivity to temperature and pressure make them a useful tool for standard conditions measurement.

Summary

The calibration and use of flow measuring devices is basic to the measurement of air pollutants. Most atmospheric measurements require the accurate knowledge of either the total volume of air or the flow rate. Many devices exist to aid in the measurement of volume and flow rate. Three types are most commonly used in atmospheric sampling—volume, rate, and velocity meters. Standard devices exist at the primary, intermediate, and secondary level.

Sample Problems

Problem 1. Volume Conversion to Standard Conditions

A volume of 20 m³ was drawn from a spirometer at 20 °C and 700 mm Hg. What was the standard volume drawn?

$$V_2 = V_1\left(\frac{P_1 T_2}{P_2 T_1}\right)$$

Where:

V_2 = *volume at condition* 2

V_1 = *volume at condition* 1 = 20 $\mathbf{m^3}$

P_1 = *pressure at condition* 1 = 700 mm Hg

P_2 = *presure at condition 2 = 760 mm Hg*

T_1 = *temperature at condition* 1 = 20 °C + 273 = 293 °K

T_2 = *temperature at condition* 2 = 25 °C + 273 = 298 °K

$$V_2 = (20\ \mathrm{m^3})\left(\frac{700\ \mathrm{mm\ Hg}}{760\ \mathrm{mm\ Hg}}\right)\left(\frac{298\ {}^\circ\mathrm{K}}{293\ {}^\circ\mathrm{K}}\right)$$

$$V_2 = 18.7\ \mathrm{m^3}$$

Problem 2. Orifice Conversion When Used at Other Calibration Conditions

An orifice was calibrated at 21 °C and 760 mm Hg. It is to be used to calibrate a sampler at conditions of 25 °C and 700 mm Hg. The flow at field conditions is 0.85 m^3/min (30 CFM): (a) What is the flow rate at calibration conditions? (b) What is the flow rate at standard conditions?

$$Q_2 = Q_1 \left(\frac{T_2 P_1}{P_2 T_1} \right)^{1/2}$$

Where:

	Part a	*Part b*
Q_2 = *Flow 2*	*(cal. condt.)*	*(STD condt.)*
Q_1 = *Flow 1*	0.85 M^3/min	Q_2 in Part a
P_2 = *Press 2*	760 mm Hg	760 mm Hg
P_1 = *Press 1*	700 mm Hg	760 mm Hg
T_2 = *Temp 2*	21° + 273° = 294 °K	298 °K
T_1 = *Temp 1*	25° + 273° = 298 °K	294 °K

(a) The flow rate at calibration conditions:

$$Q_2 = (0.85\ M^3/\text{min}) \left(\frac{700\ \text{mm Hg} \times 294\,°\text{K}}{760\ \text{mm Hg} \times 298\,°\text{K}} \right)^{1/2}$$

$$Q_2 = 0.81\ M^3/\text{min}$$

(b) The flow at standard conditions: (using orifice data at calibration conditions and the flow derived in part a)

$$Q_2 = Q_1 \left(\frac{P_1 \times 298\,°\text{K}}{760\ \text{mm Hg} \times T_1} \right)^{1/2}$$

$$Q_2 = 0.81 \left(\frac{760\ \text{mm Hg} \times 298\,°\text{K}}{760\ \text{mm Hg} \times 294\,°\text{K}} \right)^{1/2}$$

$$Q = 0.82\ M^3/\text{min}$$

Problem 3. Conversion for Different Gas Used with a Rotameter

A rotameter was calibrated with air at 0°C and 760 mm Hg. The rotameter is now to be used to add helium as a carrier gas at 0°C and 760 mm Hg. If the flow reading at point X on the rotameter corresponded to 28.3 liters/min (1 ft^3/min) when air was used, what flow will point X correspond to when helium is used? (Density of helium = 0.1785 g/ℓ and for air = 1.2929 g/ℓ

$$Q_2 = Q_1 \left(\frac{\varrho_1}{\varrho_2}\right)^{1/2}$$

Where:

Q_2 = *flow with gas* 2

Q_1 = *flow with gas* 1 = 28.3 ℓ/min

ϱ_1 = *density of gas* 1 = 1.2929 g/ℓ = *(air)*

ϱ_2 = *density of gas* 2 = 0.1785 g/ℓ *(helium)*

$$Q_2 = 28.3 \left(\frac{1.2929 \text{ g}/\ell}{0.1785 \text{ g}/\ell}\right)^{1/2}$$

$$= 28.3\ (7.2431)^{1/2}$$

$$Q_2 = 76.2 \text{ liters/min}$$

Problem 4. Pump Capacity

Can a pump with the following capacity curve (Figure 3-41) be used to drive critical orifices that have flow rates of (a) 50 cc/min and (b) 250 cc/min at criticality? (Hint: atmospheric pressure = 30 in Hg)

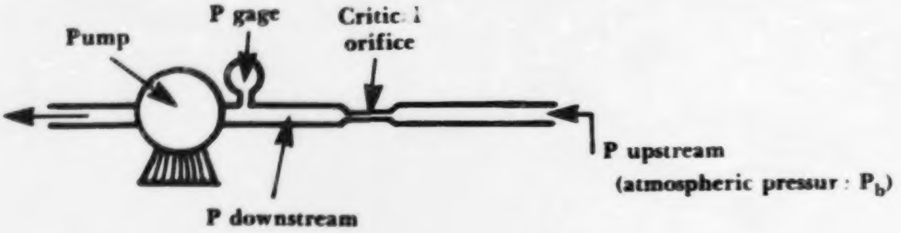
For an orifice to be critical $P_{downstream} \leq 0.53$

$$P_{downstream} \leq 0.53 \text{ or } \leq 0.53(30) \text{ or } \leq 16 \text{ in Hg.}$$

$$P_{downstream} = P_b + p_g, \text{ therefore}$$

$$p_g = 30 - 16 = 14 \text{ in Hg gage vacuum}$$

At a gage vacuum of 14 in. Hg the pump can pull approximately 130 to 140 cc/min. Therefore, this pump could operate orifice (a) at 50 cc/min but not (b) at 250 cc/min.


P gage
Critical
orifice
Pump
P upstream
(atmospheric pressure: P_b)
P downstream

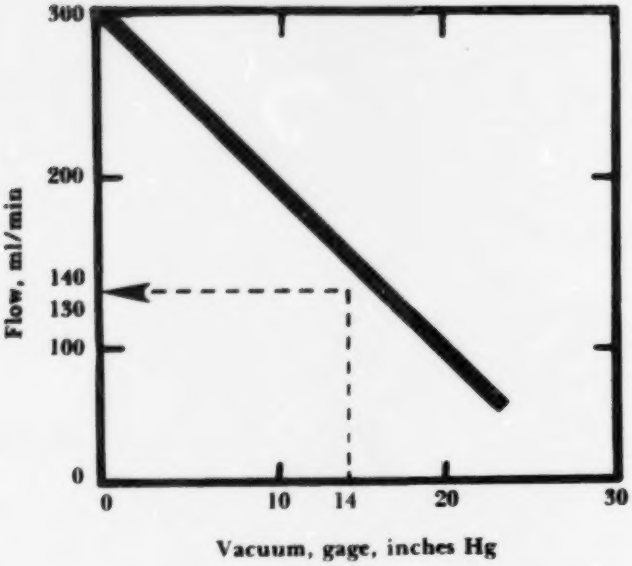


Figure 3-41. Problem 4: Pump capacity.

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Chapter 4

Particulate Sampling

Introduction

Particulate matter is one of the more noticeable forms of air pollutants. Consequently, particulates have been monitored more extensively and for a longer time than other pollutants. Particulate monitoring has been performed mostly by filtration and gravity-induced settling for many years. Studies showing that the human respiratory tract is size selective of particulates led to the development of samplers for "respirable" particles. Most "respirable" particulate samplers have relied on inertial methods to collect samples. Precipitator samplers (both thermal and electrostatic) are now of limited use in airborne particulate sampling.

The major prerequisite in the design of any sampling train is the ability to collect a representative sample. Particulate sampling trains for concentration, size distribution, and chemical composition (among other parameters) have varied and unique requirements. Optimal methods for each type of sampling are still debatable. The discussion of particulate sampling in this chapter will be limited to five collection mechanisms (gravity, filtration, inertial, inertial-filtration combinations, and precipitators) and the advantages and disadvantages of each mechanism will be discussed.

Principles of Inertial Collection

Introduction

Particle size distribution studies are of interest because of the adverse health effects of particles in certain size ranges. Very large particles (10 μm or larger) entrained in inhaled air are removed in the nose and throat, and thus do not reach the lungs. Very small particles (smaller than 0.1 μm) pass into the lungs but are exhaled and not retained in the lungs. The particles in the 0.1 - 10 μm size range are generally thought to be *respirable*. Figure 4-1 shows the depth of penetration into the lungs of particles of various size ranges.

It should be noted that particulates in the air seem to be distributed bimodally with regard to particle size (6). This distribution appears to have peaks at about 0.4 μm and 10 μm (Figure 4-2). The larger particles are those that appear naturally (dust, pollen, etc.). The smaller particles are usually manmade (anthropogenic) consisting of products of combustion or process losses (see Figure 4-3). Hence, most manmade particles are in the respirable range and are usually the particles that carry health hazards (i.e., heavy metals, polynuclear aromatics, etc.).

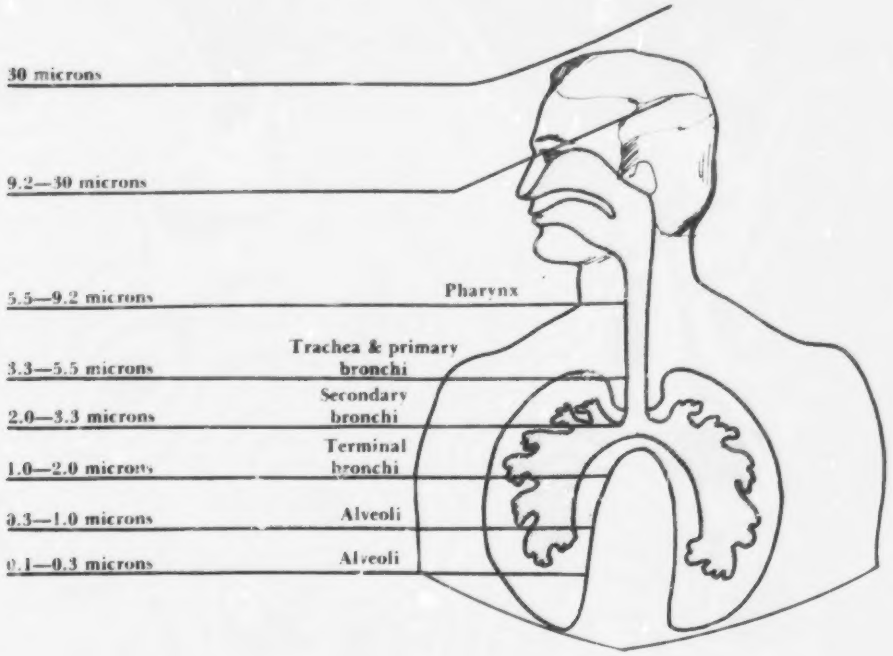

30 microns
9.2—30 microns
5.5—9.2 microns
Pharynx
3.3—5.5 microns
Trachea & primary bronchi
2.0—3.3 microns
Secondary bronchi
1.0—2.0 microns
Terminal bronchi
0.3—1.0 microns
Alveoli
0.1—0.3 microns
Alveoli

Figure 4-1. Respiratory collection of particulates.

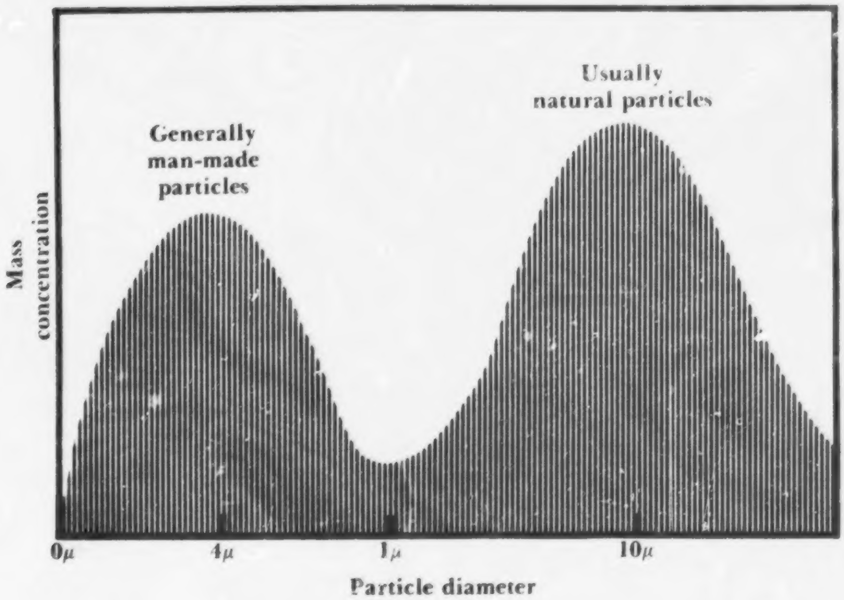
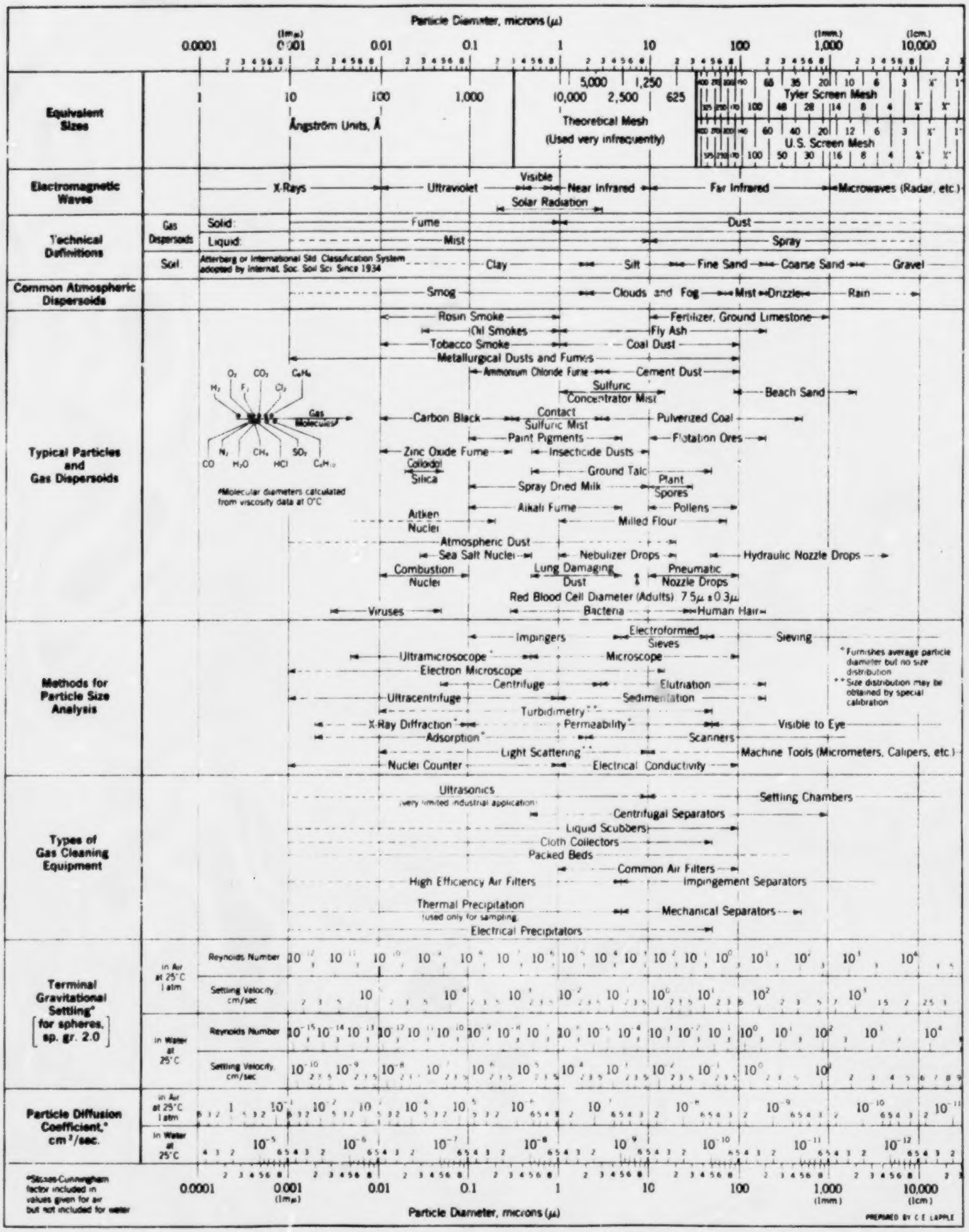


Figure 4-2. Bimodal distribution of particles in the atmosphere.

CHARACTERISTICS OF PARTICLES AND PARTICLE DISPERSOIDS



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Figures 4-3. Characteristics of particles and particle dispersoids.

Inertial collectors are designed to give a size representative sample of particulates in the atmosphere, using a method based on the fact that the particles in a gas stream are more dense than the fluid (air) in which they are suspended. A particle moving in an air stream with approximately the same velocity as the air stream has more momentum (*mass* × *velocity*) than the volume of air that it displaces because of its higher mass. The momentum, or inertia, possessed by a particle in a moving air stream will cause the particle to be deflected less than the air in the vicinity of the particle when the air stream undergoes a sudden change in direction. Such a deflection will occur when an obstacle is placed directly in the path of an aerosol stream. If the resulting deflection of the particle from the air trajectory around the obstacle is great enough, the particle will strike the obstacle. High incident velocities will increase the momentum of nongaseous materials in the air stream, thereby enhancing their removal. High velocities can be attained by passing the air stream through an orifice or jet prior to the stream striking the obstacle as in Figure 4-4.

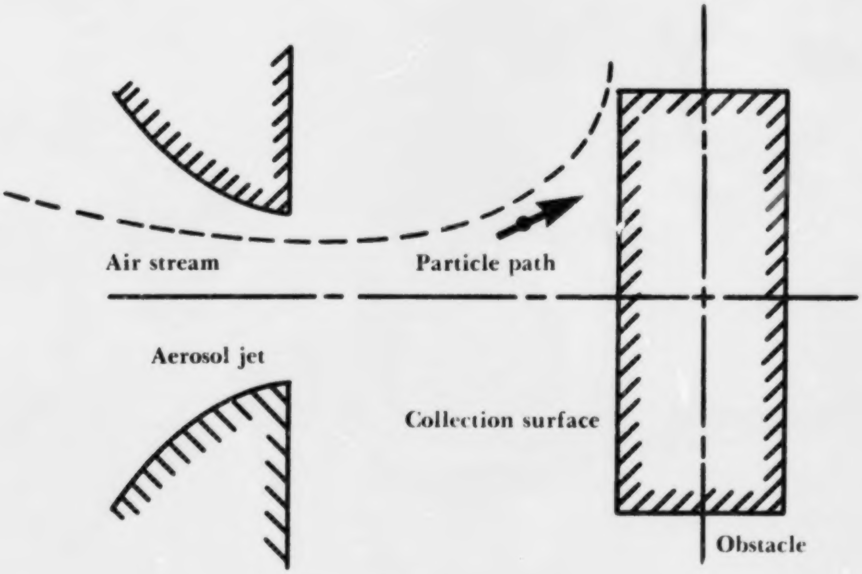


Figure 4-4. Particulate collection by impaction.

Under the proper conditions, most of the particles within a certain size range that can be made to strike the obstacle will become attached to and remain on the collection surface.

Analysis of Inertial Collection Mechanisms

A complete analysis of the inertial collection of particles in aerosols includes an analysis of the forces acting on a particle in a rapidly moving aerosol stream. The collection itself should also be examined. Collection is the phenomenon involved when a particle strikes and becomes attached to an obstacle in the aerosol trajectory.

The net force on a particle in a moving aerosol stream is the result of several forces acting on the particle. The net force can be expressed in the equation:

(Eq. 4-1)

$$-\frac{(\overrightarrow{u}-\overrightarrow{v})}{z} + \overline{mg} + \vec{F} = m\frac{d\vec{u}}{dt}$$

Where:

$\vec{u}$ = *particle velocity*
$\vec{v}$ = *velocity of air stream*
z = *"mobility"*
m = *particle mass*
$\vec{g}$ = *gravitational acceleration*
$\vec{F}$ = *electrical force*

The net force ($F = ma$) on the particle is represented by $m(d\vec{u}/dt)$.

The term $-(\overline{u}-\overline{v})$ [illegible] expression for the fluid resistance of the air to the particle flow in which z, the mobility, is a function of the particle diameter and the physical properties of the air. The term for the fluid resistance is valid under the assumption that viscous forces predominate in the particle flow through the air stream, that is, the particle is equivalent to a sphere of small diameter and the particle velocity is small. The term $\overline{mg}$ represents the gravitational force on the particle. The electrical forces acting on the particle are represented by $\vec{F}$.

In the inertial collection process, the particle is removed from the air stream as a result of a sudden change in the fluid resistance force. While the particle is traveling in the air stream prior to passing through the jet, the particle velocity, $\vec{u}$ is nearly the same as the fluid velocity $\vec{v}$. As the air stream approaches an obstacle, the air velocity $\vec{v}$ undergoes a sudden change as the fluid spreads and flows past the obstacle. The particle follows the trajectory described in the equation. At this point the gravitational and electrical forces on the particle are negligible in comparison with the momentum of the particle. Whether the particle will reach the surface of the collector depends upon the proximity of the starting position to the axis of flow through the center of the collector, the nature of the streamlines along which the particle passes, the configuration of the flow system, and the size and shape of the collector (17).

Types of Inertial Sampling Devices

The inertial collection process is subdivided into two main types, impaction and impingement. The distinction is made by the manner in which the sample material is retained in the sampling device.

Impaction Devices

Impaction devices collect and retain particles from an aerosol stream on a surface. The collecting surface is removed from the instrument and the sample analysis is, in many cases, performed directly on the collecting surface. Particle adhesion is caused primarily by electrostatic attraction and by molecular surface phenomena called Van Der Waals forces (1). Some loss of large particles occurs with high aerosol velocities. It is believed that in the case of small particles, (several micrometers or less), nearly all of those striking the collecting surface are retained on the surface. The collection surface in many impaction devices is coated with a thin film of oil or light grease to aid in particle retention. In some devices, retention is aided by passing the incoming particles through a zone of moisture saturated air; moist particles adhere more readily to a collection surface. Coating of the plates and water saturation of the particles affect the calibration of an impactor and must be accounted for if the impactor is to be used for particle size distributions.

Single Stage Impactor

A single stage impaction sampler contains one jet, or orifice, and one collection surface. The earlier, simpler devices were this type, and many of these collected a sample by the operation of a simple attached pump. An example of a single stage impactor is the Staplex Annular Impactor shown in Figure 4-5. It was designed specifically for selectively sampling dense plutonium particles in aerosols generated by various operations in the production of fissionable material.

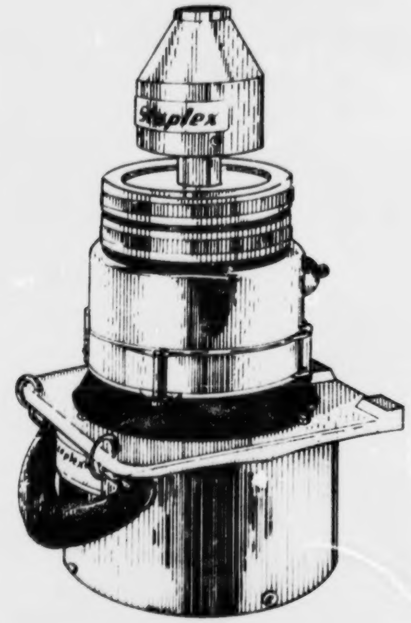
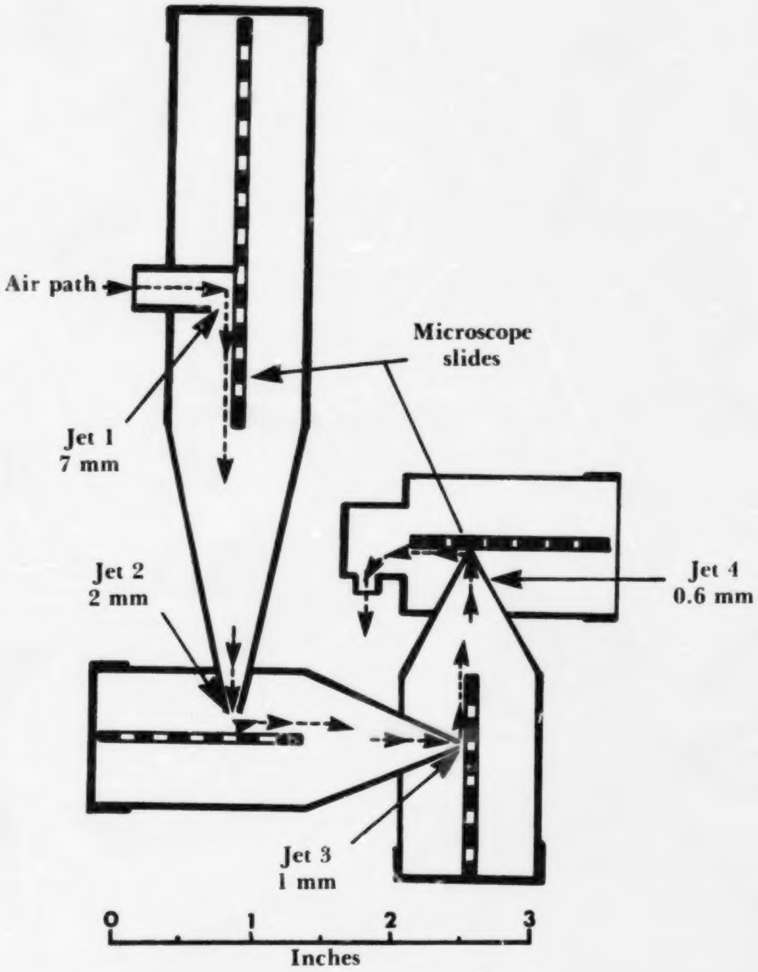


Figure 4-5. Annular impactor (courtesy of the Staplex Co.).

Cascade Impactor

A widely used impaction device is the "cascade" impactor shown in Figure 4-6. This device consists of several impaction stages arranged in series. Each successive stage contains a smaller jet placed closer to the collection surface than in the previous stage. This arrangement causes an increase in the aerosol velocity and a greater deflection angle at each stage through the sampler. The result is a higher collection efficiency for particles of decreasing size at each stage through the impactor.



Air path
Microscope slides
Jet 1
7 mm
Jet 2
2 mm
Jet 4
0.6 mm
Jet 3
1 mm
0
1
2
3
Inches

Figure 4-6. Cascade impactor schematic diagram.

A cascade impactor gives an aerosol sample that is graded into particles of sizes within slightly overlapping ranges, with one range of sizes retained on each collecting surface. The largest particles are collected on the slide opposite the first jet and the smallest particles are collected on the slide opposite the last jet. Figure 4-7 shows the collection efficiency of the cascade impactor for each stage and the particle sizes that are collected on that stage. Note the overlap between stages (i.e., stage 1 collects only 25% of the 10 μm particles but stage 2 collects 100% of the remaining 10 μm particles

Particle size (μ)		0.35	0.4	0.45	0.5	0.6	0.7	0.9	1.0	1.2	1.4	1.6	1.8	2.0	2.5	3.0	4.0	5.0	6.0	8.0	10	12	14	16	20
Capture efficiency	Stage 1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.03	0.11	0.25	0.45	0.68	0.84	1.0
	Stage 2	0	0	0	0	0	0	0	0	0	0	0.01	0.03	0.06	0.13	0.21	0.56	0.84	0.95	1.0	1.0	1.0	1.0	1.0	1.0
	Stage 3	0	0	0	0	0.02	0.05	0.13	0.18	0.28	0.43	0.66	0.87	0.96	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
	Stage 4	0.08	0.21	0.45	0.69	0.89	0.98	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0

Figure 4-7. Capture efficiencies of a

Andersen Samplers

Another example of a multi stage impactor is the Andersen Sampler. This sampler usually contains six to eight stages with successively smaller, evenly distributed holes in each stage. Each stage has numerous holes or orifices. A constant flow rate is maintained through the Andersen sampler with the result that the velocity of the gas stream increases at each stage, allowing for the deposition of particles in a fractionation by size. Each stage of the sampler consists of a perforated disc under which lies the collection medium (see Figures 4-8 and 4-9). The sample air passes through the openings in the disc and must then make an abrupt change of direction over the collection medium. The particles possessing too low a velocity to continue in the air stream are impacted on the collection surface. The collection surface can be coated with a light oil, silicone grease, filter media, aluminum foil or wax to help increase the collection efficiency. The thickness of the coating is not important, as long as it is at least the thickness of the particle that is to be collected. However, a heavy coating is not recommended since this will likely lead to the clogging of jets. Such coatings may also interfere with subsequent chemical analysis, and the collection "cut points."

The greatest limitation of the Andersen sampler is the relatively low flow rate, 0.28 cubic meters per minute (1 cfm), that must be maintained (13). Figure 4-10 shows the collection efficiency of the Andersen sampler at this flow rate.

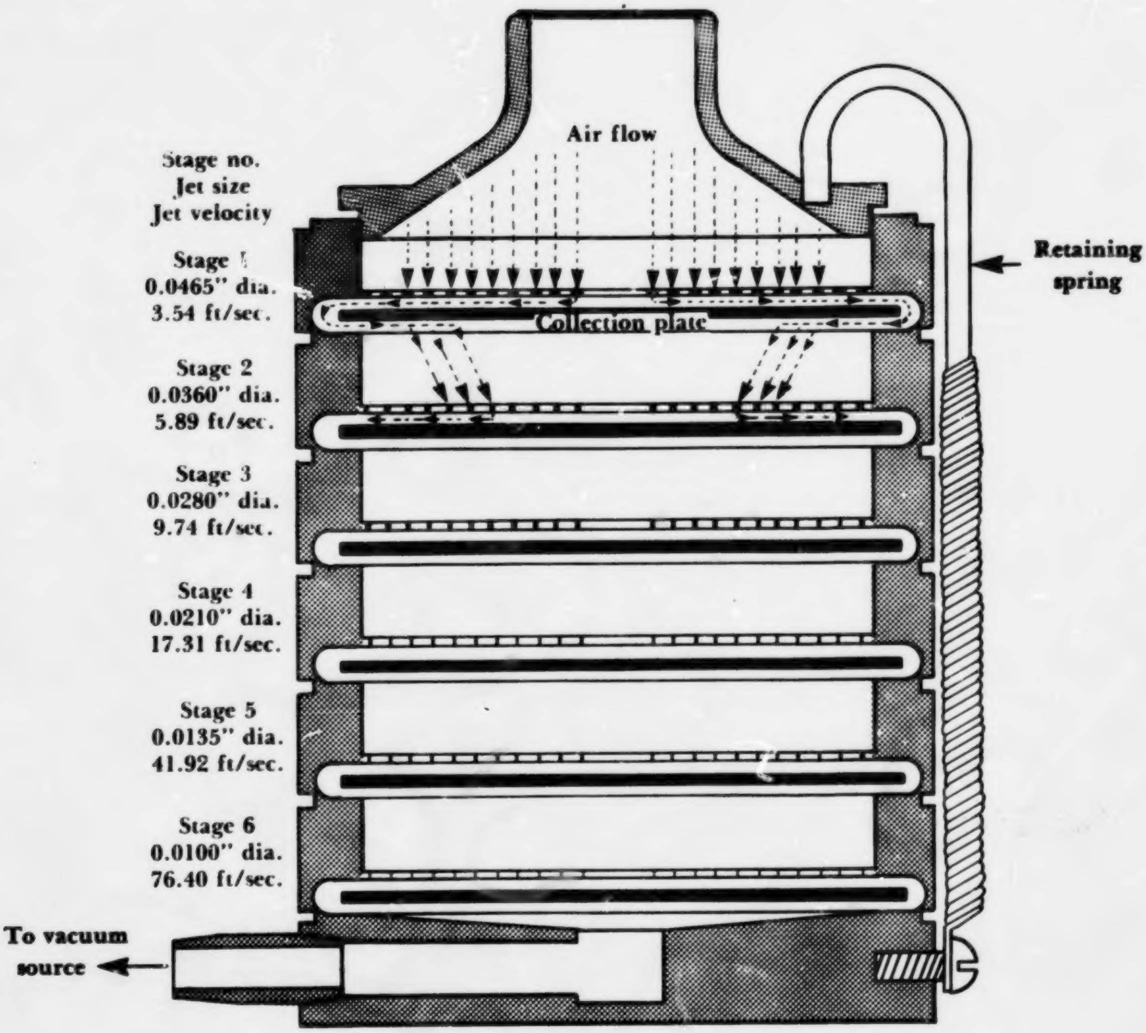

Air flow
Stage no.
Jet size
Jet velocity
Stage 1
0.0465" dia.
3.54 ft/sec.
Collection plate
Retaining spring
Stage 2
0.0360" dia.
5.89 ft/sec.
Stage 3
0.0280" dia.
9.74 ft/sec.
Stage 4
0.0210" dia.
17.31 ft/sec.
Stage 5
0.0135" dia.
41.92 ft/sec.
Stage 6
0.0100" dia.
76.40 ft/sec.
To vacuum source

Figure 4-8. Andersen sampler schematic diagram. (Courtesy Andersen Samplers and Consulting Service).

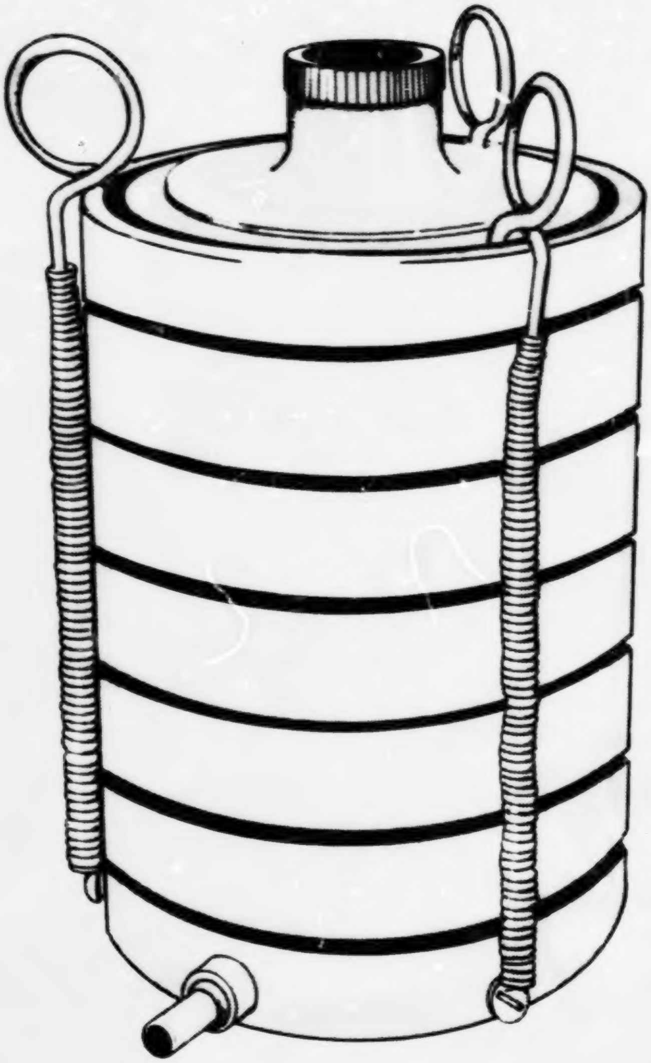


Figure 4-9. Andersen sampler.
(Courtesy Andersen Samplers and Consulting Service)

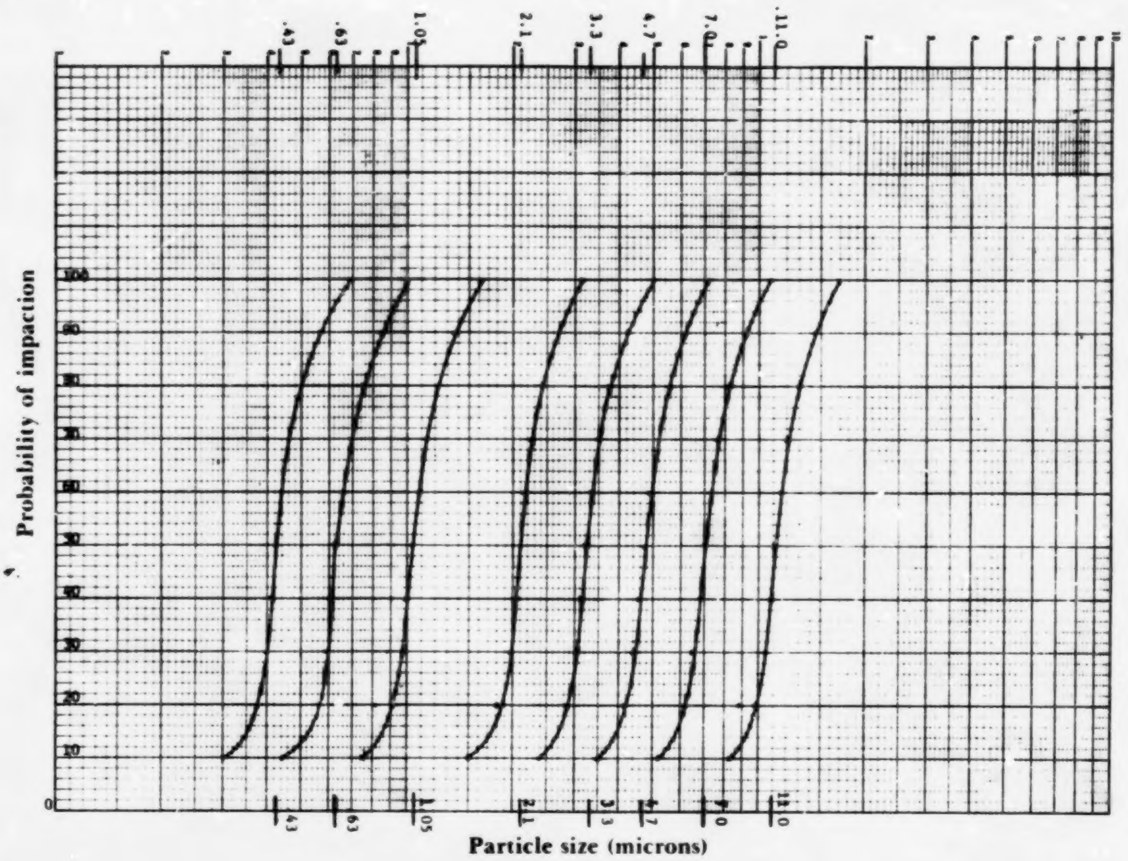


Figure 4-10. Collection efficiency of Andersen Sampler.

Modified Andersen Sampler

To overcome the low flow rate of the Andersen sampler, a modified Andersen sampler has been devised (8). This modified sampler can operate at flow rates between 0.14 and 0.17 cubic meters per minute (5.06 cfm). To modify the Andersen sampler, the sixth stage was eliminated and replaced by a 10.2 cm (4 in.) diameter filter. The filter media, commonly glass fiber or membrane filters, collect the particles that were not impacted in the previous five stages. This sampler is housed in a shelter similar to that used for a high volume sampler and is mounted above another cabinet that is used as the motor shelter (see Figure 4-11). The required motor must be capable of drawing 0.14 cubic meters per minute (5 cfm) at a vacuum of 203 mm Hg (8 in. Hg) for prolonged periods.

An advantage of both of these Andersen samplers is that the pressure drop remains relatively constant throughout a 24 hour sampling period.

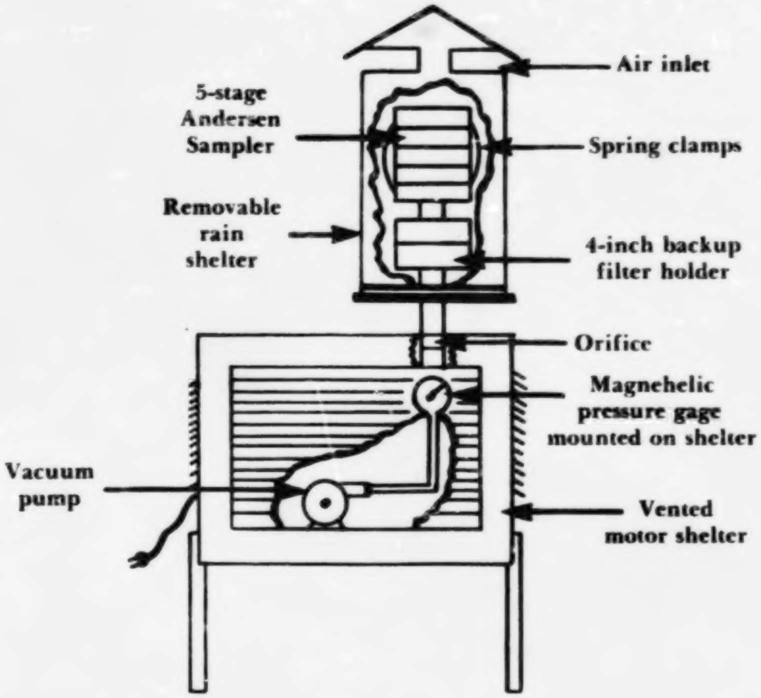

Air inlet
5-stage Andersen Sampler
Spring clamps
Removable rain shelter
4-inch backup filter holder
Orifice
Magnehelic pressure gage mounted on shelter
Vacuum pump
Vented motor shelter

Figure 4-11. Diagram of modified Andersen impactor sampler and shelter.

Figure 4-12 shows the collection efficiency of the modified Andersen sampler for each stage as well as the overlapping of particle size collection that occurs with all impactor collectors. The dotted lines represent an extrapolation of the curves that were not obtained experimentally (7).

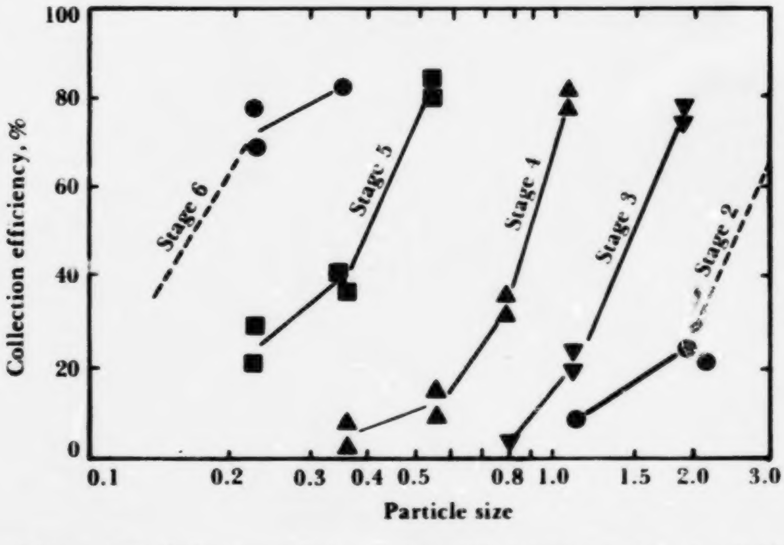


Figure 4-12. Collection efficiency of modified Andersen Sampler (3 ft^3/min).

High Volume Andersen Cascade Impactor

A further modification of the Andersen Sampler has led to the High Volume (hi-vol) Andersen Sampler, which can be used at flow rates as high as 0.57 m^3/min (20 ft^3/min). This sampler consists of five stages with the typical Andersen perforated discs. Following the discs are gaskets and collection surfaces (Figure 4-13).

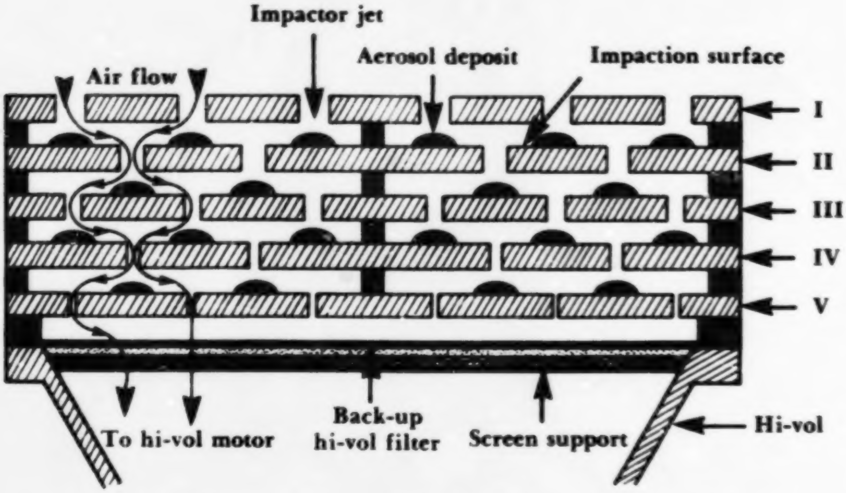

Impactor jet
Aerosol deposit
Impaction surface
Air flow
I
II
III
IV
V
To hi-vol motor
Back-up hi-vol filter
Screen support
Hi-vol

Figure 4-13a. Cross-sectional view of hi-vol Andersen impactor.

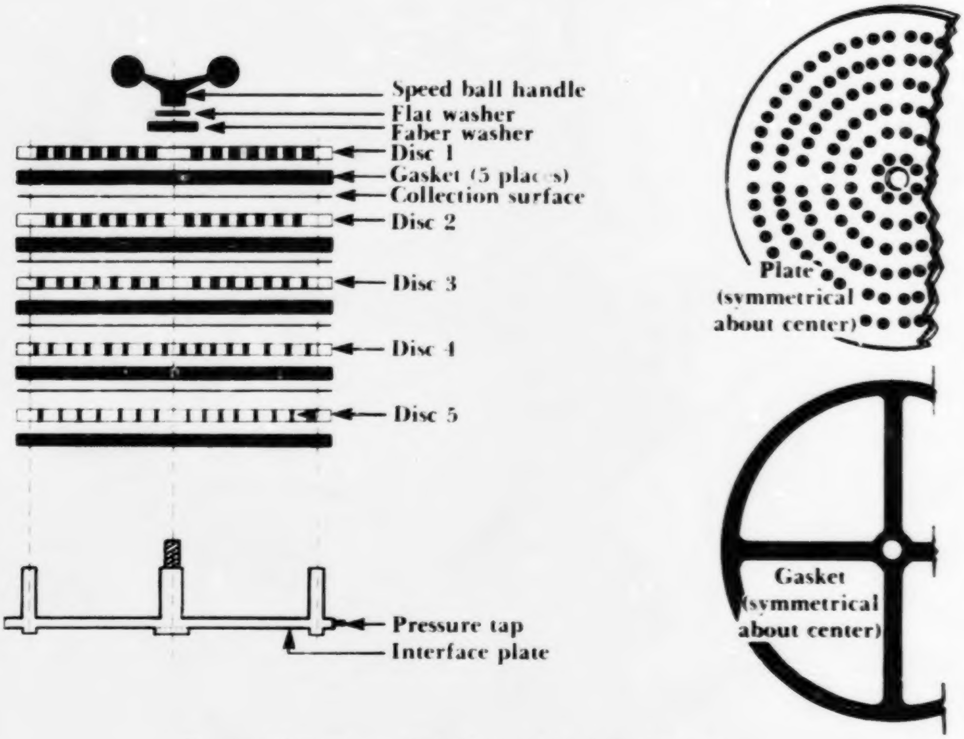

Speed ball handle
Flat washer
Faber washer
Disc 1
Gasket (5 places)
Collection surface
Disc 2
Disc 3
Disc 4
Disc 5
Pressure tap
Interface plate
Plate (symmetrical about center)
Gasket (symmetrical about center)

Figure 4-13b. Expanded view of hi-vol Andersen impactor.

The collection surfaces, usually a glass fiber filter or aluminum foil (2), are supported by the plates themselves, i.e., the collection surface for plate 1 is supported by plate 2 and so on. To allow unrestricted aerosol flow, the collection surface has holes that line up with the orifices of the plate supporting it. The five stages are held together by a central bolt and are aligned by four evenly spaced rods. The impactor is mounted on a hi-vol sampler. An 8" × 10" filter mounted on the hi-vol is the backup filter for the impactor. Figure 4-14 shows the collection efficiency of the hi vol Andersen impactor operated at 20 ft³/min.

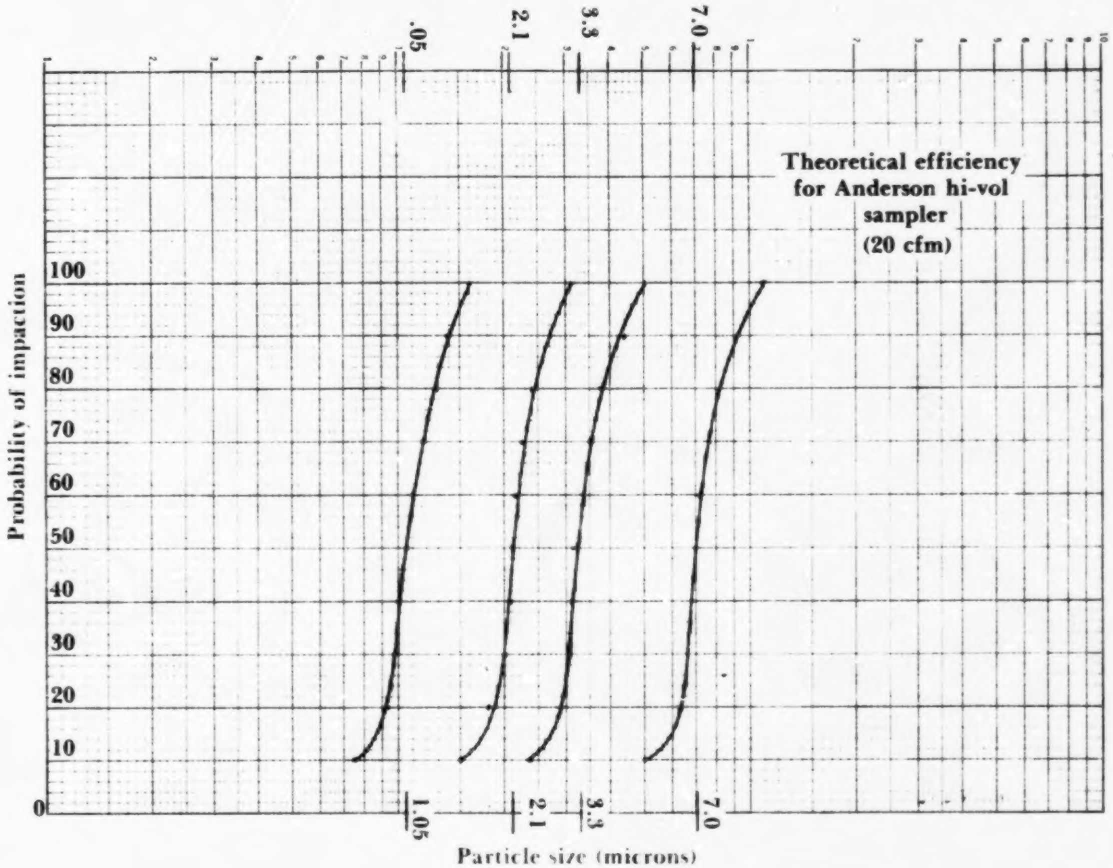


Figure 4-14. Collection efficiency of hi-vol Andersen impactor (20 ft³/min).

Multiple-Slit High Volume Cascade Impactor

Another of the size fractionating particulate samplers utilizes a typical high volume motor blower unit with an adapter comprised of four stages with successively smaller slit openings. Behind each slit is a collection plate for retaining particles. The fifth stage of this impaction device uses a typical hi vol filter for collection of small particulates.

The air is drawn through the slits and over the collection-surfaces. The slits become increasingly thinner and the velocity increases at each stage so particles of decreasing size are impacted on each successive surface. The collection plates are 5.1 cm (2 in.) wide, 12.7 cm (5 in.) long, and made of aluminum sheets 2.5 mm (1/10 in.) thick. The actual collection surface is made of glass fiber or other materials typically used in hi-vol sampling to permit the same type of chemical analyses to be done.

The distance from the slit opening to the collection surface becomes smaller with each stage to increase the collection efficiency (see Figure 4-15).

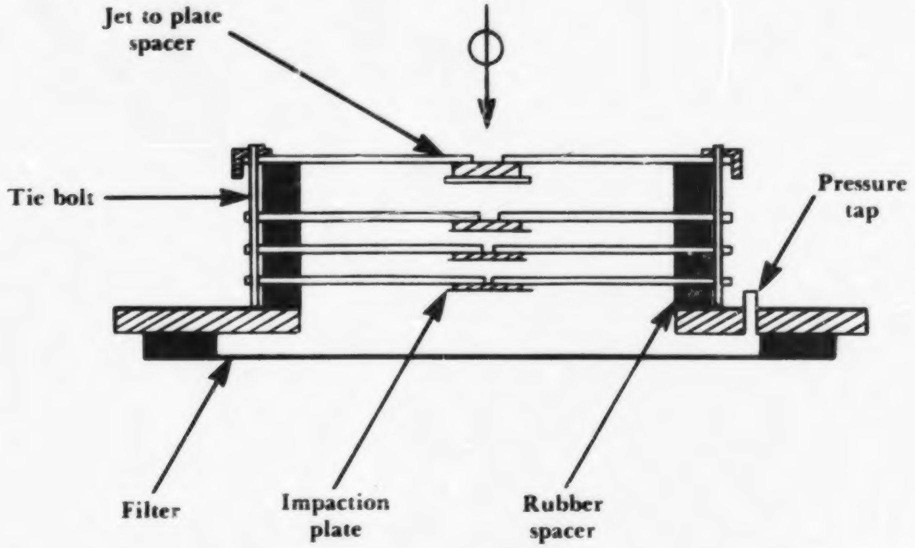


Figure 4-15. Multi-slit high-volume cascade impactor.

One advantage of this impactor unit is that it will fit over the existing hi-vol sampler used in most particulate networks. This will minimize the costs involved in purchasing equipment to complete a size fractionating particulate network. Another advantage is the high flow rate, 0.85 cubic meters per minute (30 cfm) (4). More recently, 40 cfm has been achieved with limited losses (19). This incorporates the advantages of hi-vol sampling (high flow rates and, therefore, large sample size) and the advantages of impactor sampling (determination of the size fraction of the atmospheric particulates). Figure 4-16 shows the percent penetration, which is related to the collection efficiency, of different sized particles and the impactor stage. The greater the percent penetration, the lower the collection efficiency.

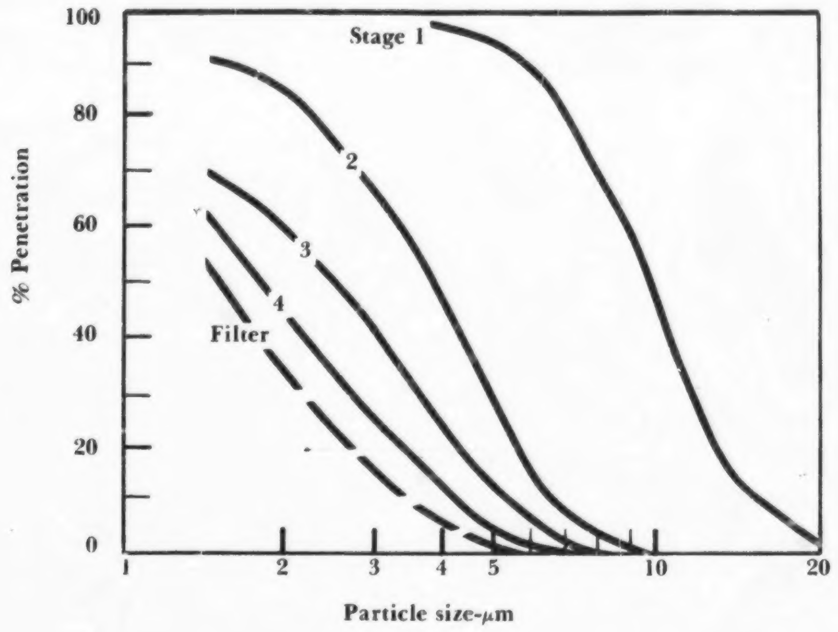


Figure 4-16. Penetration vs. particle size.

Lundgren Sampler

The Lundgren sampler is designed to give a concentration determination based upon not only particle size but also time (11). The sampler consists of four nozzle openings, consecutively decreasing in size. Behind each of the nozzle openings is a rotating drum (see Figure 4-17). By rotating the collection drum, the concentration of each size particle can be determined as a function of time. The drums of the Lundgren sampler are driven by a motor, and the rotational speed can be varied by changing the gear ratios between motor and collection surface. The Lundgren sampler has been designed to sample at a flow rate between 0.014 and 0.23 cubic meters per minute (0.5-8 cfm) while maintaining a system pressure drop of only 50 mm Hg (1.97 in. Hg). The rotating drum maintains a constant system pressure drop because there is no massive particulate buildup on the collection surface. This rotational movement also decreases the amount of sample lost due to wall losses.

With conventional hi vol samplers and cascade impactors, a mass of particles is collected throughout the sample period and only an average concentration over that period can be determined. The Lundgren sampler will not only give a size fractionation but will show how the concentration of each size of particle varied over the sample period.

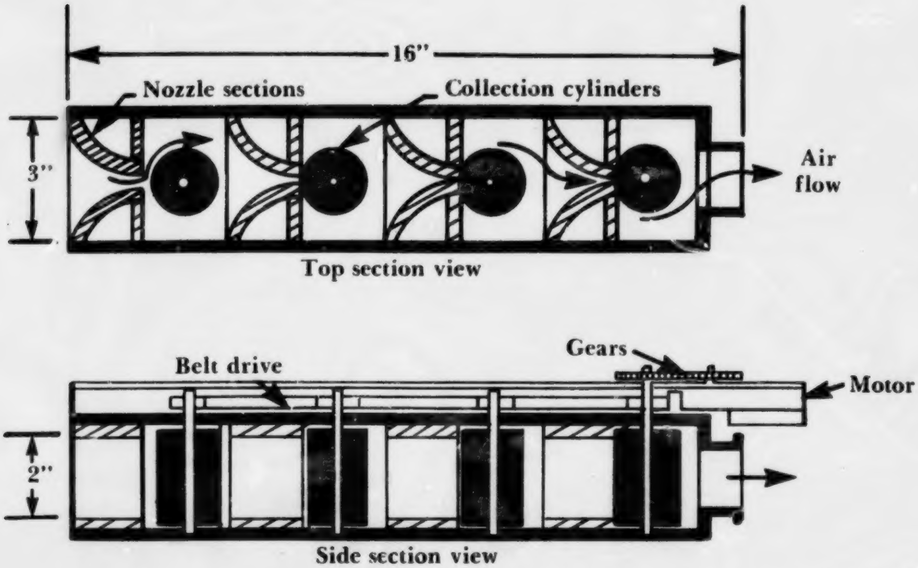


Figure 4-17. Lundgren type inertial collector.

Impingement Devices

Impingement devices differ from impactors in that the jet and striking surface are immersed in a collecting fluid such as water. The particles that are removed from the aerosol stream are wetted by and retained in the fluid. Most impingers in use are variations of the instrument developed by Greenburg and Smith (1). The Greenburg Smith type of impinger is constructed as a glass cylinder with a small concentric glass tube insert. The jet and impingement plate structure, also made of glass, are attached to one end of the tube, which is immersed in the collecting fluid. These impingers collect a sample at flow rates of about 0.1 to 1 cubic feet per minute depending on the mode of operation.

Impingers are most commonly used in collecting atmospheric samples for dusts, mists, and fumes in the evaluation of occupational health hazards. In addition to the collection of soluble gases and particulates, the Greenburg Smith impinger is an efficient collector of insoluble particles greater than two micrometers in diameter (3).

Centrifugal Separation Devices

Centrifugal separation is a variation of the inertial collection process in which particles are removed from an air stream by the centrifugal force created by moving an aerosol rapidly through a circular path.

There are several types of sampling devices employing the principle of centrifugal separation.

Cyclone Samplers

Samplers called cyclones, or miniature cyclones, are small versions of the large cyclones used in air cleaning applications. The cyclone shown in Figure 4-18 contains no moving parts and is designed so that air drawn through the cyclone will move in either a circular or a helical path of decreasing radius through the device in order to increase the collection efficiency of small particles. The gas stream surges through the cyclone and the particles are separated at the inside surface of the cyclone wall by the centrifugal force created. In most cyclone samplers the particles stick to the walls or drop into a collection space below the cyclone chamber.

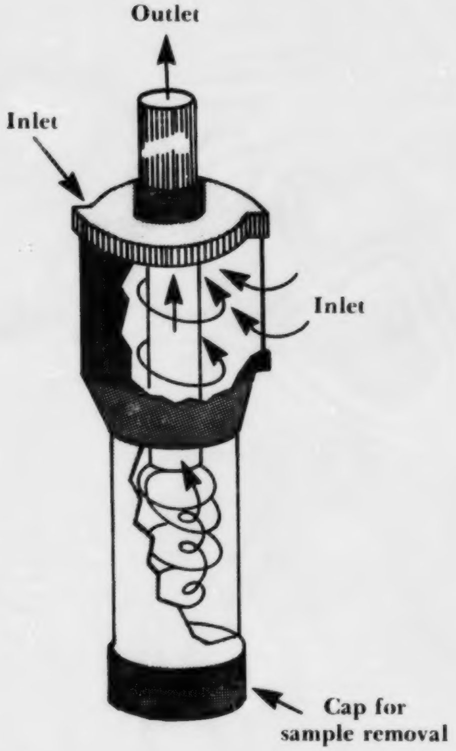


Figure 4-18. Cyclone sampler.

Most available cyclones are not efficient collectors of particles with diameters less than 2 or 3 micrometers, depending on the particle density. However, small cyclones can be designed to collect particles below 1 micrometer in diameter. The collection efficiency of a cyclone sampler is strongly dependent upon flow rate.

Spiral samplers are similar to the cyclone in having no moving parts. The air follows a spiral path and the particles are deposited on the outside wall of the spiral on a removable collection surface.

Air Centrifuges

In an air centrifuge device for aerosol sample collection, the air passes between two concentric cones. The inner cone is rotated by a motor and draws air in at the narrow upper end of the cones and exhausts the air at the large end of the cones (see Figure 4-19). The sample is collected on the inside surface of the outer cone, which may be lined with a removable collection surface. The inner rotating cone, in one model, is channeled in the form of a spiral and the outer cone spins with the rotor cone (1); laminar flow is maintained in the channels in this manner. The particles are deposited on the wall of the outer cone in the stationary boundary layer where they are protected from shear (16). The speed of rotation of the rotor cone can be varied, and it is possible to collect particles with effective diameters as small as 0.03 micrometers (1).

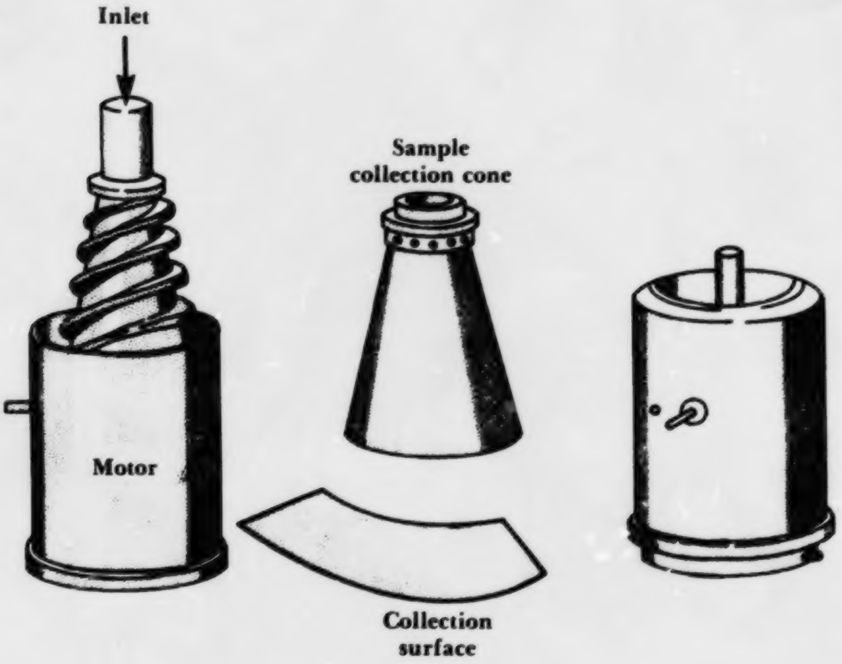


Figure 4-19. Air centrifuge.

Air centrifuges differentiate between particles according to size. The larger particles have a shorter length of deposit than do the smaller ones. The length of deposit refers to the maximum distance along the sample deposit on the collection surface which includes particles of a given size. All particles of the same size are not removed at one point. Each particle size exhibits a maximum penetration distance into the collection path.

Thus, some small particles are deposited with the large particles so that analysis by subtraction is necessary when studying size distribution (16).

Virtual Impactors—Dichotomous Sampler

In the virtual impaction method, instead of having the larger particles impacted onto a solid collection surface, they are impacted into a slowly pumped void and collected on a filter later down stream. Thus, particles larger than the 2.5 micron cut-point impact through a non-existent, or "virtual" surface. As pictured in Figure 4-20, the smaller ("fine") particles follow the streamlines of the faster flow **(F_f)**; whereas, the larger ("coarse") particles are impacted into the slower flow **(F_c)**. A small fraction of the fine particulates are impacted and collected with the coarse particles. Corrections for this can be easily made for both the fine and coarse particulates with the following equations (21):

(Eq. 4-2)

$$c_f = \frac{m_f}{t f_f}$$

(Eq. 4-3)

$$c_c = \frac{m_c - \left(\frac{m_f f_c}{f_f}\right)}{t(f_f + f_c)}$$

Where:

c_f and c_c = the atmospheric concentrations of the fine and coarse particle fractions, respectively in $\mu g/m^3$
m_f and m_c = the masses collected on the fine and coarse particle filters, respectively in μg
f_f and f_c = the flow rates through the fine and coarse particle filters, respectively in m^3/min
t = the sampling time in minutes (normally 120 min.)

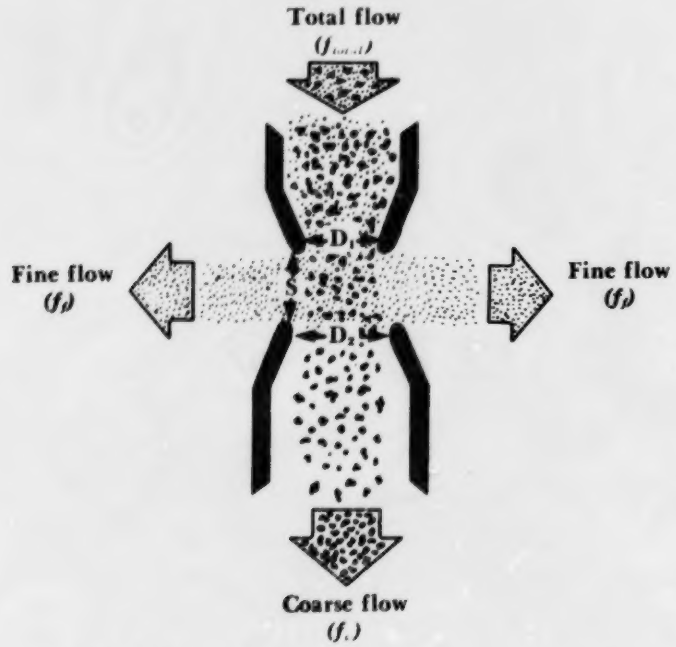


Figure 4-20. Schematic diagram of virtual impactor—critical impaction parameters are noted.

The most recent use for virtual impaction has been in EPA's efforts to develop a particulate sampler that will separate and collect particulate matter above and below a 3.5 μm aerodynamic diameter. These efforts have led to the development of the dichotomous sampler. The dichotomous sampler obtains its name from its function of sampling fine (<3.5 μm aerodynamic diameter) and coarse (>3.5 μm aerodynamic diameter) on separate filters (see Figure 4-21). The sample inlet design shown in Figure 4-22 rejects particles with an aerodynamic diameter greater than 20 μm. This inlet design has been shown to be insensitive to wind direction.

Virtual impactors have several advantages over conventional impactors (20):

- Problems associated with conventional impactors, particle bounce and reentrainment, non-uniform deposition, cumbersome sample handling, are essentially eliminated.
- Uniform deposition onto a filter medium is ideally suited for photo-excited X-ray fluorescence (a non-destructive chemical analysis technique) and beta gage mass measurement.
- No grease or oil is needed to improve collection efficiency.
- Choice of collection media (i.e., filter material) can be made to eliminate interferences.

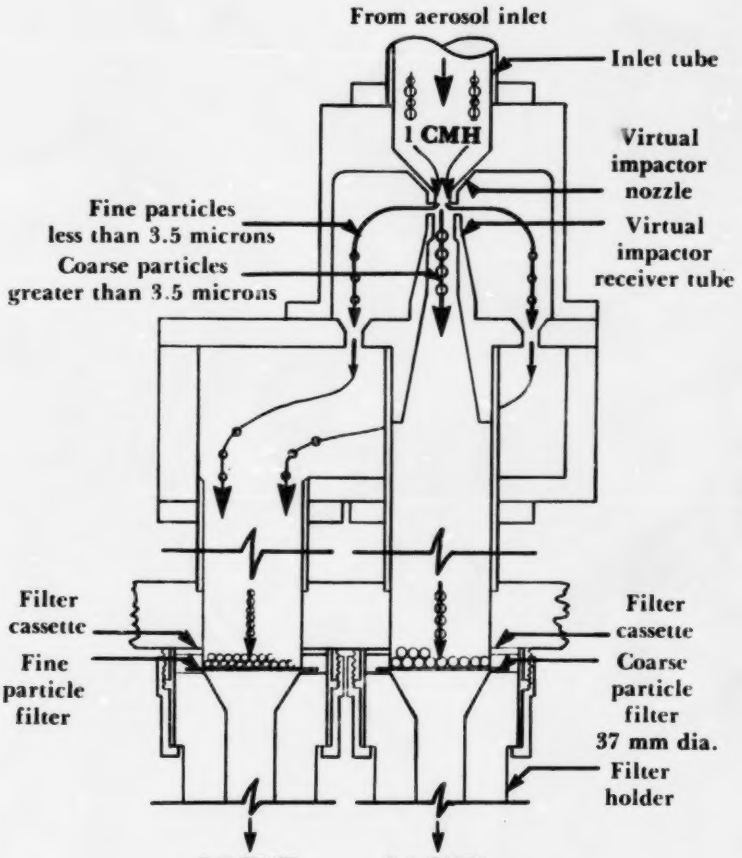

From aerosol inlet
Inlet tube
1 CMH
Virtual impactor nozzle
Fine particles less than 3.5 microns
Virtual impactor receiver tube
Coarse particles greater than 3.5 microns
Filter cassette
Filter cassette
Fine particle filter
Coarse particle filter 37 mm dia.
Filter holder
0.9 CMH
0.1 CMH

Figure 4-21. Diagram of a dichotomous sampler.

Measurements have shown that particle loss is essentially eliminated in the 1 to 2.5 and 4.5 to 20 μm ranges. The loss curve peaks at 5 percent for particles in the vicinity of 3.5 μm.

Figures 4-23 and 4-24 picture a manual dichotomous sampler that is presently being marketed. An automatic version has also been developed that changes the fine and coarse filters at pre-set time intervals.

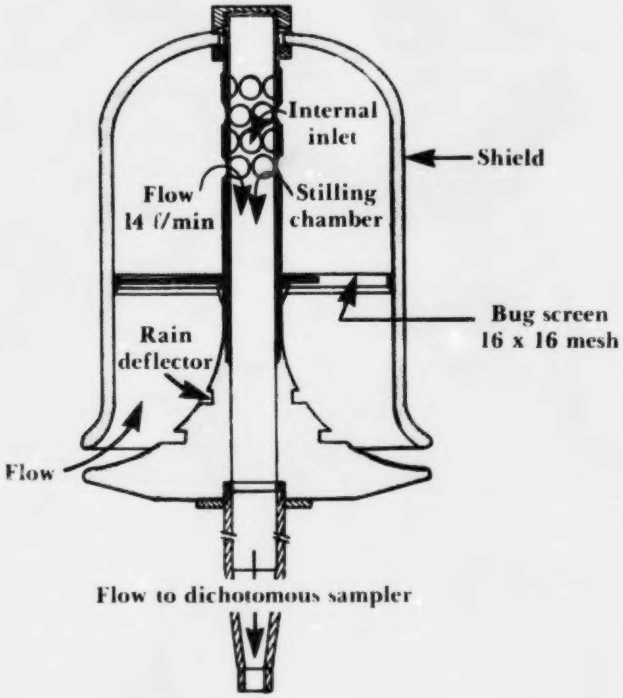


Figure 4-22. Aerosol inlet for dichotomous sampler.

The filter material used in both the coarse and fine sections is high porosity Teflon® with a 1 μm pore size. This filter material was chosen because of its several advantages over other types (22):

- Collection efficiency for particles above 0.01 μm greater than 99 percent;
- Extremely stable mass for high gravimetric accuracy;
- Negligible tendency to absorb or react with gases (therefore, low artifact formation of nitrate and sulfate);
- Minimal impurities to interfere with analyses for chemical and elemental species;
- Low mass per unit area (desirable for gravimetric, X-ray fluorescence, and β-gage measurements).

These Teflon® membrane filters will not support themselves; therefore, they are bonded to a polyethylene net or a thin annular polyester ring. The polyester ring seems to be the best choice. Investigations are being made to develop a Teflon® filter with a 2 to 5 μm pore size with high collection efficiency. These new filters would allow longer sampling periods and greater loading without clogging.

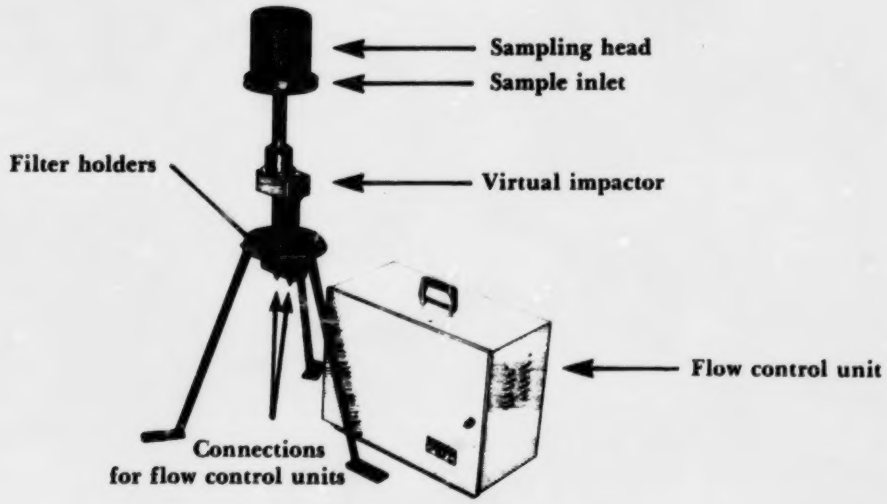

Sampling head
Sample inlet
Filter holders
Virtual impactor
Flow control unit
Connections
for flow control units

Figure 4-23. Dichotomous sampler.

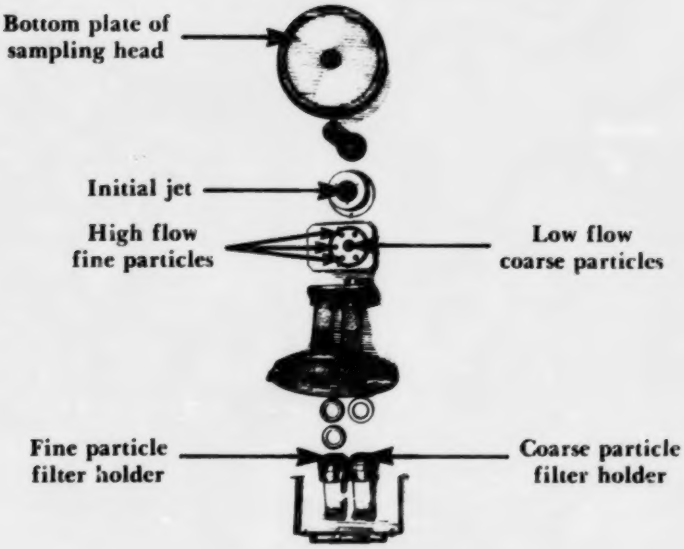
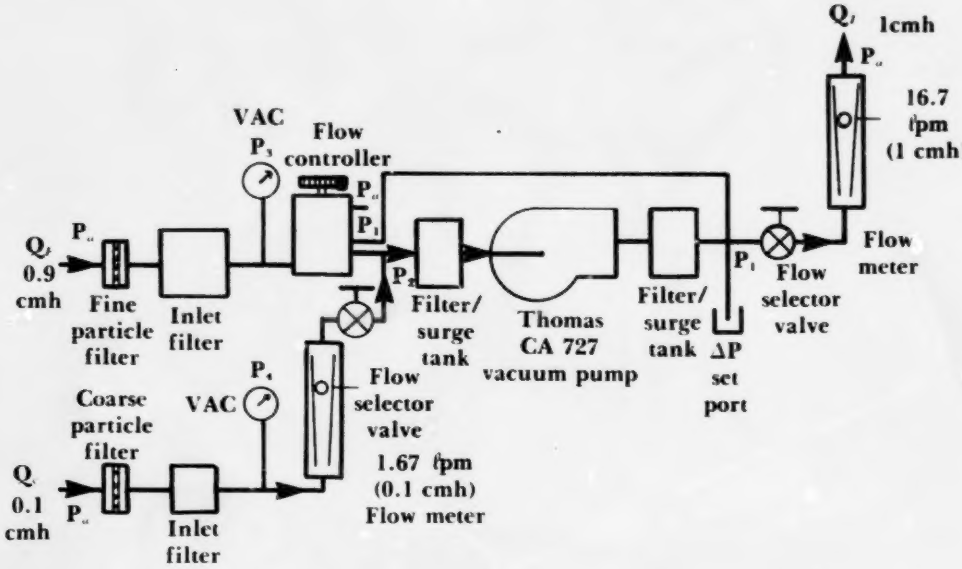

Bottom plate of
sampling head
Initial jet
High flow
fine particles
Low flow
coarse particles
Fine particle
filter holder
Coarse particle
filter holder

Figure 4-24. Expanded view of dichotomous sampler.

A constant flow rate must be maintained through the dichotomous sampler if it is to be used for quantitative procedures. The use of a differential pressure regulator in the exhaust seems to be the most rugged and promising technique to control flow. This method of flow control is used in at least one commercially available instrument (see Figure 4-25).



Q, 1cmh
P.
16.7 lpm (1 cmh)
VAC
P3
Flow controller
P.
P1
Q, 0.9 cmh
P.
Fine particle filter
Inlet filter
P2
Filter/ surge tank
Thomas CA 727 vacuum pump
Filter/ surge tank
P1
ΔP set port
Flow selector valve
Flow meter
P4
VAC
Flow selector valve
Coarse particle filter
Q. 0.1 cmh
P.
Inlet filter
1.67 lpm (0.1 cmh) Flow meter

Figure 4-25. Flow schematic of control module.

Respirable particulate sampling is becoming a major objective of atmospheric monitoring. The dichotomous sampler may possibly replace high volume sampling because of its ability to sample for fine, coarse, and total particulates, without many of the problems associated with hi-vols.

Collection Efficiency

Though the principle of collection is the same for all types of inertial sampling devices, the parameters are somewhat different for the basic single stage or cascade impactor than for the air centrifuge or cyclone. The discussion in this section is confined to the jet type of impactor, and this discussion may not be applicable without modification to other types. In this section discussions of particle size refer to the equivalent aerodynamic particle size or diameter (Stokes' diameter) unless otherwise stated. The equivalent diameter is the diameter that a unit density particle of spherical shape would have if it behaved the same as the particle being studied (9).

Definition of Collection Efficiency

Particle collection efficiency for inertial sampling devices has been defined in several ways by various people. The collection efficiency of an impaction device is a function of several parameters, making the theoretical and empirical expressions that have been derived somewhat difficult to use for specific applications. Ranz and Wong (17) showed that the efficiency of impaction was a function of an inertial parameter *I*, defined as follows:

(Eq. 4-4)

$$I = \frac{C\,[\text{illegible}]\,{}_p^2}{18\mu d_c}$$

Where:

v_o = *initial velocity of aerosol through jet*
D_p = *effective particle diameter*
d_c = *width of jet*
μ = *air viscosity*
ϱ_p = *particle density*

and *C* was defined as, "an empirical correction factor for the resistance fluids opposed to the movement of small particles, and is dimensionless. For air at normal room temperature and pressures

$$C = 1.000 + \frac{(0.16 \times 10^{[\text{illegible}]})}{D_p}$$

"The physical significance of *I* may be taken as the ratio of the stopping distance, in this case the ratio of the distance of particle penetration into still air when given an initial velocity, V_o, to the diameter or width of the aerosol jet" (1).

The collection efficiency of an impaction device can be defined as the ratio of the number of particles striking an obstacle to the number that would strike if the stream lines were not deflected (3).

For the purposes of this discussion, *the collection efficiency will simply be defined as the fraction of the particles in an incident aerosol stream that are retained on the collection surface of the sampling device*. The efficiency of impaction can be plotted as a function of *I*, the inertial impaction parameter, to give an efficiency curve for an impaction device. Studies on the calibration of cascade impactors are available (23).

Impactor Performance Characteristics

Instead of plotting efficiency of impaction against *I*, it can be plotted against particle size for a given device, since *I* is a function of particle size and several other parameters. The efficiency of impaction when plotted against particle size follows a sigmoid (or S-shaped) curve such that there is a minimum size below which no particles are collected and a maximum size above which all particles are collected. For a well designed impactor, the range between these two sizes is sufficiently narrow that a functional size separation is made (16). The most effective way to describe the ability of an impactor stage to separate particle sizes is to show the efficiency of collection as a function of size, as shown in Figure 4-26 (16).

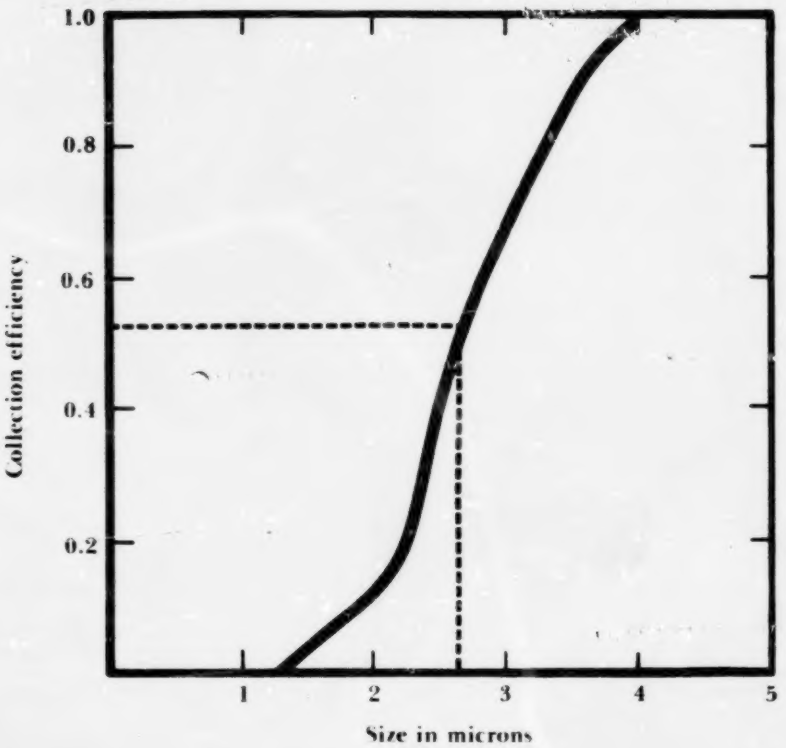


Figure 4-26. Efficiency of collection as a function of size.

Where the efficiency function crosses the 0.5 collection efficiency point is the D_{50} or "50% cutoff size." Larger particles are collected with more efficiency and smaller particles penetrate with more efficiency.

The inverse of the collection curve is the penetration curve. The size distribution of particulate on any stage is determined by the penetration curve of the stage ahead and its own collection curve. To get the actual size distribution on the stage, the efficiency and penetration values are multiplied into the size distribution curve of the incoming aerosol. The reverse operation, when the size distributions on the stage are known, gives the distribution of the incoming aerosol (16). The 50% cutoff value does not depend upon the size distribution of the aerosol being supplied to the impactor as would be true of the ***MMD (mass median diameter)***. The *mass median diameter* is that diameter above which and below which exist 50% of the collected particulate mass. It is truly valid as a characteristic of a sampler only when the aerosol sampled by the sampler has the same size distribution as the aerosol used for calibration. Since this restriction is not true of the efficiency curve, this curve is now considered by many to be the best description of sampler performance (16).

Properties of Aerosols Affecting Inertial Collection Efficiency

For a given collection device several properties of the *aerosol* affect the efficiency of collection.

Particle Size

For any device there is a minimum particle size below which no particles are collected and a maximum particle size above which all particles are collected or removed from the sampling stream. Above 50 micrometers some particle loss occurs by impaction on the walls of the sampling device. Particles and droplets greater than about 200 micrometers seldom are found on the sample collection area but are shattered or lost on the walls. Particles below about 0.5 micrometers in diameter are difficult to collect with impaction devices because their momentum is not appreciably different from that of the air, and they are not readily deflected. Most impacting devices have a high collection efficiency for particles with diameters greater than 0.5 micrometers. Collection efficiencies of nearly 100 per cent are claimed for several impaction devices for particles in the size range from 0.5 to 10 micrometers (3).

Particle Density

Impaction devices are efficient collectors of high density particles; they have been used to selectively sample work atmospheres for plutonium dusts. Sub-micrometer particles of high density can be efficiently collected, since they are equivalent to unit density particles of much greater size.

Aerosol Fluid Properties

The physical properties of the gas in which the particulate is dispersed will affect the collection efficiency of an inertial collector. The most important factor in this category influencing inertial collection efficiency is inversely proportional to the viscosity, so that a factor affecting the viscosity, such as temperature, will in turn affect the collection efficiency.

Properties of the Collecting Device Influencing Collection Efficiency

Impactors and impingers are designed for sampling a variety of aerosols. The efficiency of collection for a certain aerosol can be optimized by design considerations.

Jet Size

The impactor jet size will influence the collection efficiency by affecting the velocity with which the incident air stream strikes the collection surface. As jet size decreases, the impaction velocity increases as shown by the relationship

(Eq. 4-5) $$v = Q/A$$

Where v = air velocity
Q = volumetric flow rate
A = cross-sectional area of the air stream

In a multistage impaction device, jet velocities range from several meters per second in the first stage to greater than 50 meters per second in the last stage. The corresponding jet cross sectional areas range from about 70 mm^2 in the first stage to less than 5 mm^2 in the last stage in a typical multistage impaction device.

Many multistage impaction devices are operated at a flow rate of around 18 liters per minute. This approximates the human respiration rate. The flow rate affects the collection efficiency of a device as well as the characteristics of the sampler.

Jet Shape

Studies of impaction efficiency showed only small differences in collection efficiency between round and rectangular jets (17).

Jet to Collection Surface Distance

The distance between the jet opening and the collection surface controls the degree of deflection of the aerosol stream. By decreasing the distance between the jet and the collection surface, the angle of deflection of the aerosol stream is increased. A large deflection angle is required to remove the smaller particles from an aerosol stream. In the common cascade impactor with a single jet at each stage, the distance from the jet to the collection surface is decreased at each successive stage.

Collection Surface

Detailed studies of collection efficiency as a function of the shape of the collecting surface have been performed for spherical, cylindrical, and flat surfaces with round and rectangular shapes (17). For most applications, flat collection surfaces are used because particle retention is greatest on these surfaces and microscope slides are often required in collections for particle size analysis.

Some Applications of Inertial Sampling Devices

Gross Sampling

Under certain conditions an inertial sampling device may be the most appropriate to use in collecting a gross sample of an aerosol. Conditions such as high temperature or humidity may eliminate the use of other types of sampling devices. Inertial devices are efficient samplers of hot, moist aerosols and droplets that are likely to be encountered in stack sampling, as the moisture aids in the sample retention on the collection surface.

Size Distribution Studies

In many cases where impaction is used for aerosol sampling, the particle size distribution is of interest. This can be studied by microscope sizing and counting. Autoradiographic studies have been performed in conjunction with microscopic analysis of radioactive aerosols. When microscopic analysis is used, it is desirable to collect the sample directly on the viewing surface. The loss of particles or alteration of the sample in transferring from collecting surface to viewing surface is thus avoided. Many impaction devices use microscope slides as collection surfaces.

Theoretically, particles with diameters less than about 0.25 micrometers cannot be resolved using light microscopy. Electron microscopy can be used for size studies of particles less than 0.25 micrometers in diameter. An impactor sample for electron microscope sizing is collected directly on a fine mesh, carbon-covered, copper viewing grid (14).

The classification produced by impactors has certain advantages for microscopic determinations of size distributions when there is a large variation in particle size. Furthermore, this classification provides a technique for obtaining mass distribution curves. The impactor must be calibrated to determine the smallest particles collected at each stage or, preferably, the size of particles which are sufficiently small that they are collected with only 50% efficiency at each stage. The dust whose particle size distribution is to be determined is then collected with the impactor. The weight of material collected at each stage is determined and the results are plotted as cumulative weight distribution curves. The particle diameter corresponding to the 50% fraction is called the Mass Median Diameter (***MMD***)

Respirable Dust Sampling

To study the hazard to humans from inhaled dust particles, it is desirable to know which portion of an aerosol actually penetrates and is retained in the lower portion of the lung. To relate airborne concentrations to the amount actually deposited in the lower portions of the lung, it is necessary to sample by a technique that collects only the segment of an aerosol that is deposited in the lower portion of the respiratory system. "Respirable dust" has been defined as that portion of the inhaled dust deposited in the non-ciliated portions of the lung (3). A recent discussion of "respirable" dust sampling has been published by Lippmann (24). Samplers have been designed that closely follow the deposition characteristics of the human lung. Figure 4-27 lists the respirable percentage of several particle sizes obtained from experiments performed on humans (7).

Size in microns particles of unit density	Percent respirable
≥ 10	0
5	25
3.5	50
2.5	75
≤ 2	100

Figure 4-27. Respirable percentages of different particle sizes.

A respirable dust sampler must have a collection efficiency equal to the percentage respirable for the various particle sizes. Some respirable dust samplers utilize inertial principles in their design. A typical sampler is constructed with two stages: a first stage consisting of an inertial device (cyclone collector) that simulates the upper respiratory tract in the removal of large particles: and a second stage consisting of a membrane filter that collects the smaller particles that pass through the first stage (see Figure 4-28). The first stage must have a collection efficiency curve for particle size that allows the respirable fraction, or a close representation thereof, of the various particle sizes to pass through. When the sampler is operated at the proper flow rate, the portion collected on the membrane filter should represent the dust deposited in the lower respiratory tract. High volume cascade impactors and the newly developed dichotomous sampler are examples of samplers used in monitoring networks for respirable dust sampling.

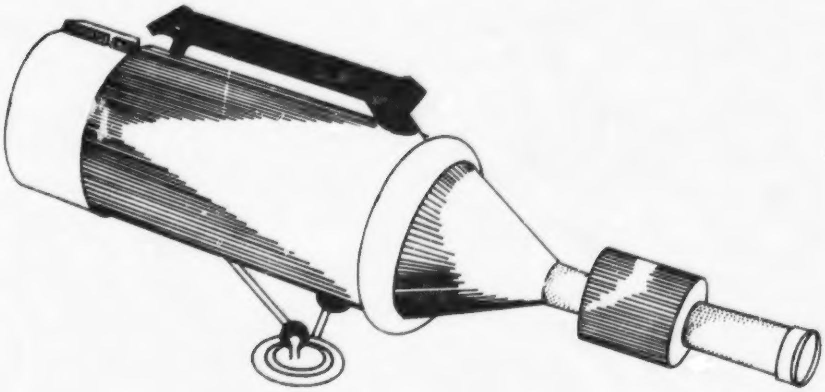


Figure 4-28. Respirable dust sampler (courtesy of Union Industrial Equipment Corp.)

Limitations and Sources of Error in Inertial Collection (Disadvantages)

Inherent Errors in Sample Collection

In many cases it is impossible to characterize a system without altering the system by the act of measurement itself. In other words, do the particles collected in an impactor sample fairly represent the dust as it is suspended in the air? There are several inherent sources of error in the impaction process.

Particle Shattering

Large particles (greater than 200 micrometers) and agglomerates are readily shattered upon impaction, and, at the high velocities attained in some impaction devices, particles with diameters as small as two or three micrometers can be shattered. In studies where the number of particles per unit volume of air is of interest, shattering of particles upon collection results in erroneously high results. In size distribution studies, there will appear to be fewer large particles and more small particles than actually exist in the aerosol. Figure 4-29 is a picture taken from an electron microscope of a shattered fly ash particle.

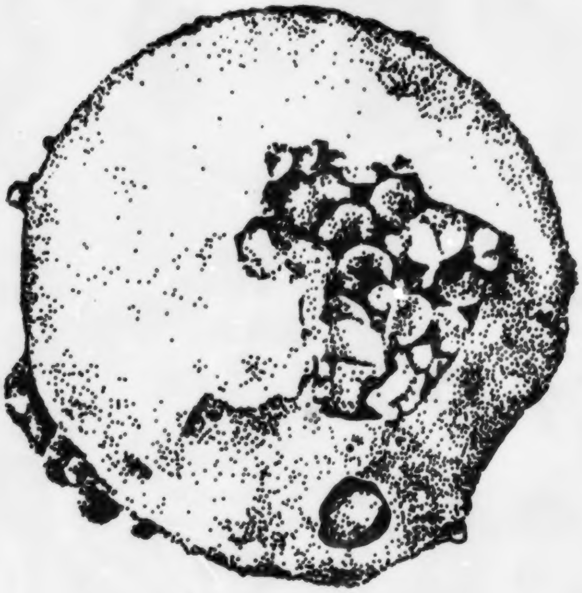


Figure 4-29. Particle shattering.

Particle Bounce, Re-entrainment of Particles, and Wall Loss

At high impaction velocities a small fraction of the particles collected may be re-entrained in the air stream. This occurs most often with fragments of large particles that have shattered upon striking the collection surface. Some of the pieces of the shattered particles may be lost from the sample by impacting on the walls of the instrument. A few of the large particles may impact directly on the walls of the instrument.

If the instrument is not thoroughly cleaned prior to use, particles that have impacted on the walls in previous sampling may become re-entrained in the aerosol stream within the instrument and be collected on the collection surface.

Particulates can also become re-entrained because they bounce when they strike the collection surface. Dzubay, et. al. experimentally showed that the "...nature of the impaction surface can have a severe distorting effect on the size distribution which one measures with a cascade impactor" (25).

Limited Sample Quantity

The small quantity of sample collected also restricts the choice of analytical methods to those with high sensitivity. Care must be taken to preserve all sample material intact, since with only a few micrograms of sample, the loss of any particulate becomes significant.

Some types of inertial samplers, such as cyclones, are not so limited in this respect. Some of these can collect gram quantities of particulates.

Nonrepresentative Sample Collection

If jet impactors are used in sampling high concentrations of particles or mists, the time of sample collection must be short in some applications. If too much material is collected, the sample will be useless for size and mass distribution.

Sample Loss in Collection

If too much particulate material collects on the sample collection surface, subsequent particles that impact may be lost by re-entrainment when they strike particles already collected instead of the collection surface.

A phenomenon called "ghost depositing" can occur when particles bounce off the collection area and are redeposited by eddy currents a few millimeters on either side of the sample.

When aerosols containing mists or droplets are being sampled, care must be taken to avoid collection of too much material. If too many droplets are collected, they will merge on the collection surface. The individual drops will be lost for size analysis and some material may be lost by run-off.

Poor Particle Resolution for Size Analysis

Particles that collect close to and on top of each other will introduce error in concentration and size studies through the inability to distinguish between individual particles and clumps of particles when examined optically. However, if a representative portion of the collected material is properly remounted in a preparation, these problems can be minimized.

Errors Associated with the Calibration of Collection Devices

When impactors are used to collect aerosol samples for particle size or mass distribution studies, the instrument must be calibrated. The particle collection efficiency as a function of the desired parameter, (e.g., size or mass) must be determined. One method of calibration is to empirically determine the collection efficiency in the laboratory. In this procedure a known quantity of a monodisperse aerosol (a gas stream with only 1 size particle suspended in it) is passed through the impactor. The amount of material collected on each stage is weighed. By varying the size of the monodisperse aerosol the cutoff points for each stage can be determined. Detailed studies of theoretical collection efficiencies for several types of impaction devices have been performed (3). The efficiency curves that have been derived for several types of impactors show varying agreement with experimental curves. These curves are usually given in terms of an inertial collection parameter or equivalent particle size such as the one in Figure 4-10. If a particular curve is to be used in a sampling application, the user should be satisfied that the curve is valid for that particular application. Most commercially available inertial samplers are provided with a curve of collection efficiency. In most cases the methods used to obtain these curves will not be known to the user. Care should be exercised in the application without specific knowledge of the manner in which the curves were obtained (23).

Errors in Sample Analysis

Investigations of radioactive aerosols, and aerosols in general, in which the sample is collected with an inertial collection device may utilize any of several kinds of sample analysis. The analyses that are performed on samples collected by impactors may also be used in conjunction with other sampling methods and are discussed elsewhere. Mention of the error associated with the analytical procedure to be used is made because it should be considered in the overall error assessment of the sampling procedure. The information desired in an investigation may require the use of an inertial collection device, which in turn may limit the choice of analytical procedure. The reverse could also occur, i.e., the information desired such as particle size distribution, may dictate the use of an impaction device to collect the sample. One should be aware of the limitations and error associated with each analytical procedure that is considered.

Summary

Inertial sampling devices have found numerous applications in the study and monitoring of atmospheric aerosols. Though not used as frequently as some other types of sampling devices, inertial samplers are superior for certain applications. The investigator can choose from a number of available devices with different performance characteristics. A wide range in cost and degree of sophistication are exhibited by these devices. An understanding of the principles involved as well as the limitations and sources of error is a prerequisite for the achievement of valid results in any investigation using inertial samplers.

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High-Volume Air Sampling

Introduction

When air pollution control agencies attempt to determine the nature and magnitude of air pollution in their communities and the effectiveness of their control programs, they collect samples of suspended and, sometimes, settleable particulate matter.

Several different sampling techniques and devices filtration, electrostatic and thermal precipitation, and impaction – may be employed to collect suspended particulate pollutants from ambient air. Of the various techniques, filtration has been found to be the most suitable for routine air sampling. The so-called, high-volume (hi-vol) sampler is generally accepted as the instrument of choice for this purpose. Approximately 20,000 high-vols are operating at Federal, State, and local air pollution control agencies, industries, and research organizations for either routine or intermittent use. The number is growing rapidly as air monitoring programs expand.

The Environmental Protection Agency has designated the High-Volume method as the reference method for total suspended particulates (TSP) (24). Certain situations, e.g., sampling for State Implementation Plans (SIP) and Prevention of Significant Deterioration (PSD), require the organization responsible for sampling to use the reference high-volume method when determining TSP.

Development of the High-Volume Sampler

In 1948 Silverman (16) developed an aerosol collector that consisted of a household vacuum sweeper motor encased in an airtight sheetmetal housing adapted to hold a 4-inch diameter filter. Provision was made for measuring the air flow through the system. Because this sampler operated at a much higher flow rate than other available samplers, it was identified as a high-volume sampler and the designation persists. Replacement of the thin sheet-metal motor housing with one of cast aluminum by the Staplex Company* in the early 1950s improved the Silverman sampler. Adoption of a stainless steel filter holder to accomodate an 8 by 10-inch filter permitted 24-hour operation of the sampler and collection of a much larger sample of particulate matter than previously possible (see Figure 4-30).

Although the Staplex sampler performed satisfactorily, it was decided after several years of experience that a more rugged sampler was needed to meet the requirements of a large scale sampling network operation. Accordingly, in 1957 a new high-volume sampler (11), developed in collaboration with General Metal Works, was introduced. The new sampler used a different motor that was completely enclosed in a cast aluminum housing, eliminating the sheetmetal and rubber components used in the Staplex sampler thus simplifying brush and motor replacement. This sampler is widely accepted. Other high-volume samplers, some of which embody slight modifications, have been marketed recently.

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*Mention of company or product by name is for identification and information purposes only and does not constitute endorsement by the Environmental Protection Agency.

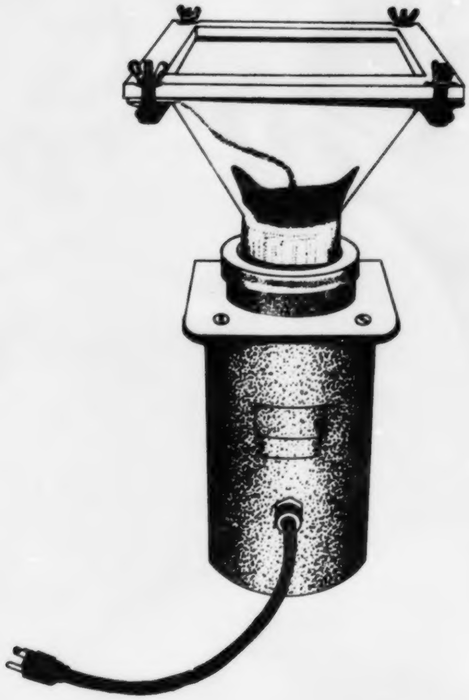

Figure 4-30. Hi-vol sampler.

Equipment

Sampler-Shelter Combination

The sampler and its shelter should be considered as a single, functioning unit (see Figure 4-31a). The shelter must provide protection for the sampler, and at the same time allow unrestricted access of ambient air from all directions without direct impingement of particles on the filter. A high-volume sampler with a 7 × 9-inch exposed filter area operated in a standard shelter at 50 to 60 cubic feet per minute (1.4 to 1.7 cubic meters per minute) collects particles up to 100 microns in size and uniformly distributes the sample over the filter surface. The standard peak roof of the shelter, which acts as a plenum above the filter, is placed to provide a total opening area of slightly more than the 63-square-inch filter area, thereby permitting free flow of air into the plenum space (see Figure 4-31b). Any deviation from the size of the opening to the filter or the volume of air filtered per unit time will affect the particle size range collected. Distribution of particles on the filter may also be affected.

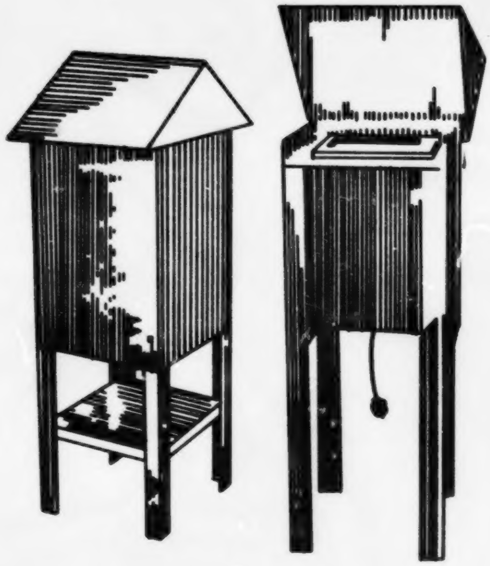

Figure 4-31a. Hi-vol sampler with shelter.

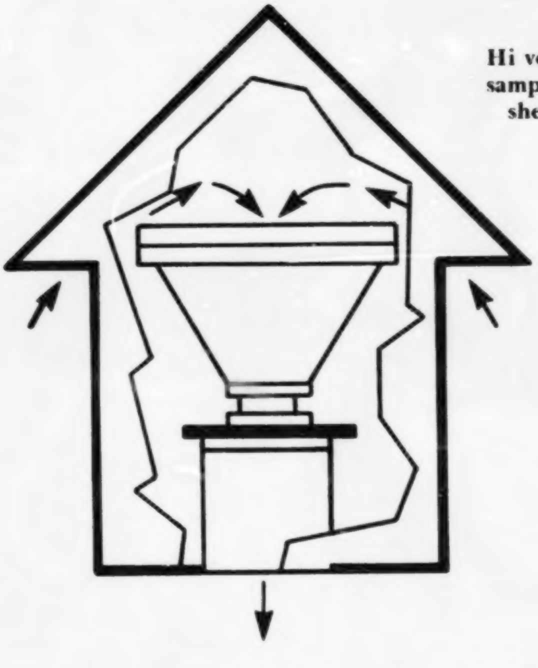
Hi volume
sampler in
shelter

Figure 4-31b. Air flow of hi-vol sampler in shelter.

Filter Media

Choice of filter media is influenced by the objectives of the sampling program and the characteristics of the sampler to be employed. Results of a comprehensive study of the characteristics of different types of filter media were published in 1964 by Lockhardt and Patterson (7). An excellent discussion of filter media and filtration sampling is presented in *Air Sampling Instruments* (23).

Glass fiber filters, although not perfect in all respects, have been found to meet most of the requirements for routine particulate sampling. Such filters have a collection efficiency of at least 99.9 percent for particles of 0.3 micrometers and larger, low resistance to air flow, and low affinity for moisture, all of which are distinct advantages during sampling. However, in order to eliminate possible weight errors due to small amounts of moisture, both clean filters and samples should be equilibrated at 20° to 25°C at a relative humidity below 50 percent for 24 hours before weighing. Figure 4-32 shows the effect of moisture on the weight of glass fiber filters. Figure 4-33 shows the effect of moisture on the weight of particulate matter.

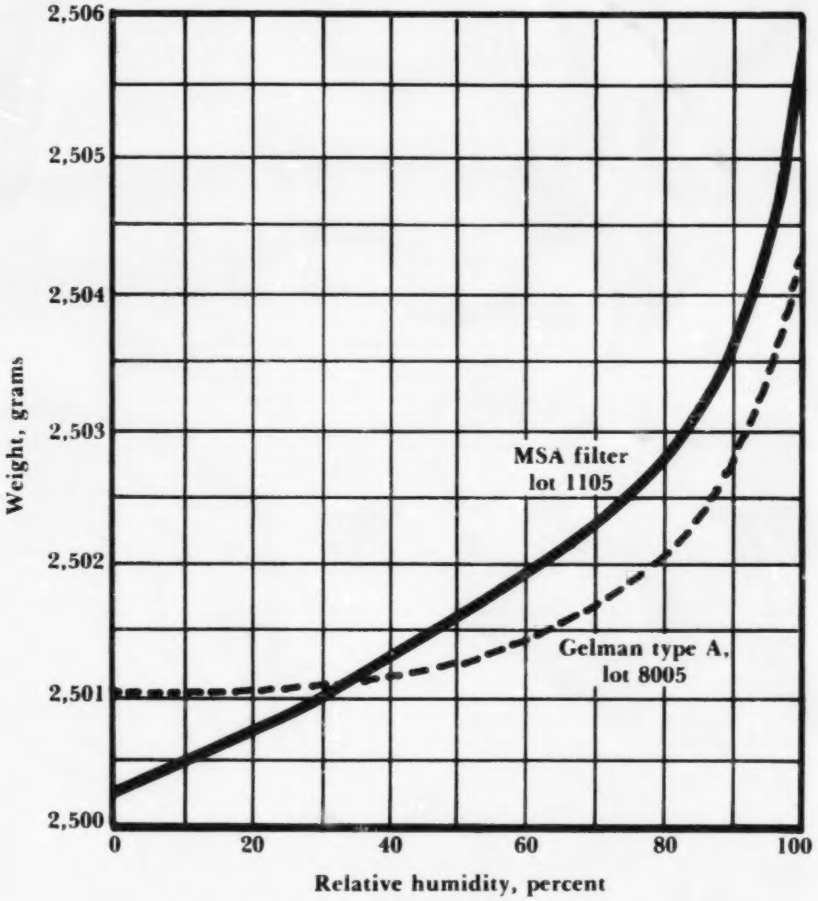

Figure 4-32. The effect of relative humidity on the weight of glass fiber filters at 75°F.

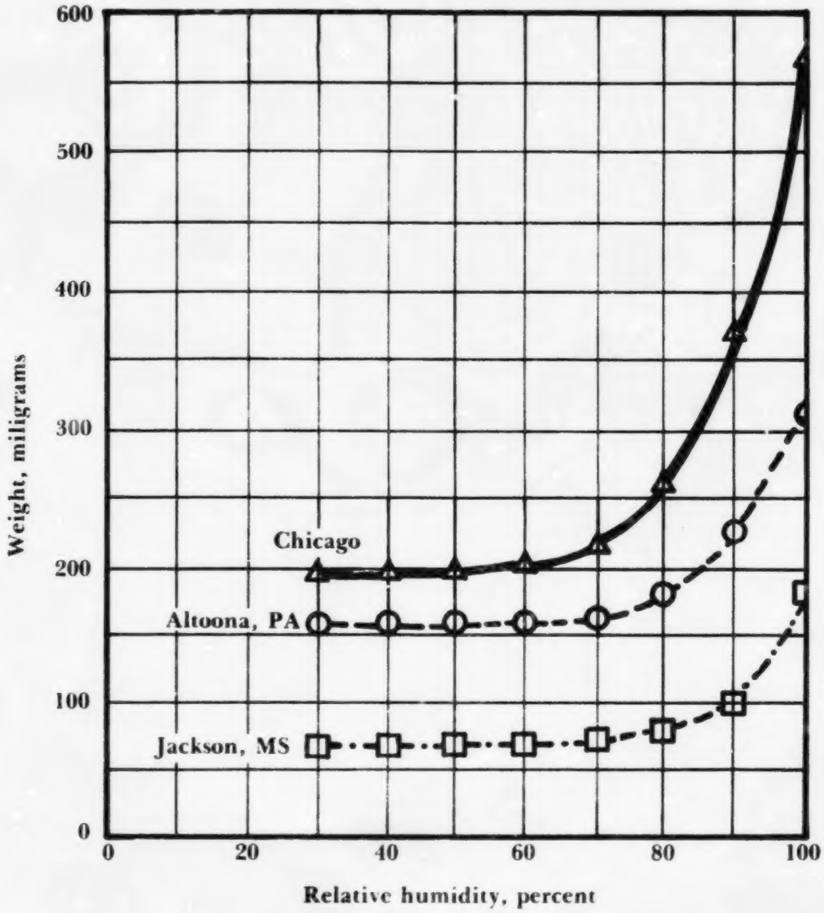

Fig. [illegible] The effect of relative humidity on the weight of atmospheric particulates at 75°F.

Samples collected on glass fiber filters are suitable for analysis of a variety of organic pollutants (13, 19, 20, 25, 26) and a large number of inorganic contaminants (18, 21, 27) including trace metals and several nonmetallic substances. Glass fiber filters are excellent for use in monitoring gross radioactivity (6, 15). It must be pointed out, however, that because of filter composition, satisfactory analyses for silica, calcium, sodium, potassium, lead, zinc, and other materials present in substantial amounts in the filter are not possible. Recent work has produced an acceptable glass fiber filter for metals analysis (29). Particulate samples can be analyzed for a variety of organic pollutants including benzo(a)pyrene, ammonia (from ammonium salts), nitrates and sulfates, (however, artifact formation may be a problem) fluorides, antimony, arsenic, beryllium, bismuth, cadmium, chromium, cobalt, copper, iron, lead, manganese, molybdenum, nickel, tin, titanium, and vanadium. A random but statistically significant sample of new filters should be analyzed to determine what the filter blank concentration is and whether or not it is high enough to interfere with a particular analysis. It is wise to obtain this information before purchasing large numbers of filters to avoid potential problems caused by high blanks. Results of studies of the analytical aspects of glass fiber filters in air pollution were reported by Pate and Tabor (10) and Little (30).

While glass fiber filter material has been dominant in the measurement of total suspended particulate, numerous applications have been found for cellulose filters. Cellulose filtering media has relatively low metal content making it a good choice for metals analysis by neutron activation, atomic absorption, emission spectroscopy, etc. Conventional high-volume samplers usually have to be modified to use cellulose filters because cellulose filters clog rapidly causing flow to sometimes decrease by as much as a factor of two during a one-day sample (31, 32). Other disadvantages of cellulose are its irreversible absorption of water (33) and enhanced artifact formation of nitrates and sulfates. These disadvantages can usually be overcome by using a control blank filter. Spectro-quality grade glass fiber filters have sufficiently low background metal contents to make them acceptable for metal analysis, if cellulose cannot be used.

Precautions in Filter Handling

After the desired filter material has been chosen, it should be inspected visually for holes and tears that may cause uneven loading, loss of particulate, and failure during the sampling period. The aid of a light table may be used to better determine the quality of the filter paper. A number should be assigned to each filter to create better data handling. Care should be taken not to tear the filter when affixing the identification number.

Before the weighing of the filter paper, the filter should be equilibrated in a conditioning environment (20° to 25°C not to vary more than ± 3%, relative humidity less than 50% not to vary more than ± 5%) free of acidic or basic gases that might react with the filter media. The analytical balance used for the weighing should be calibrated with standard weights between three to five grams (the average clean filter weight should be in this range). The filters should be taken directly from the conditioning chamber to the weighing area to minimize the risk of contaminating the filters. Then they should be weighed to the nearest milligram, and the weight and the number of each filter recorded. The filter must not be folded or creased before use as this may establish erroneous flow patterns during sampling.

To install a clean filter in the sampler, the wing nuts are loosened and the faceplate is removed. The filter should be centered and the gasket should be placed so that equal spacing of the filter is held by the gasket. The faceplate is then replaced and the wing nuts tightened. The gasket should not be tightened to the point where filter damage might occur. Hi-vol filter cartridge assemblies similar to the one pictured in Figure 4-34 make installation of filters easier. Installation and removal of a filter can be performed inside a building thus eliminating handling problems due to lack of space and windy conditions.

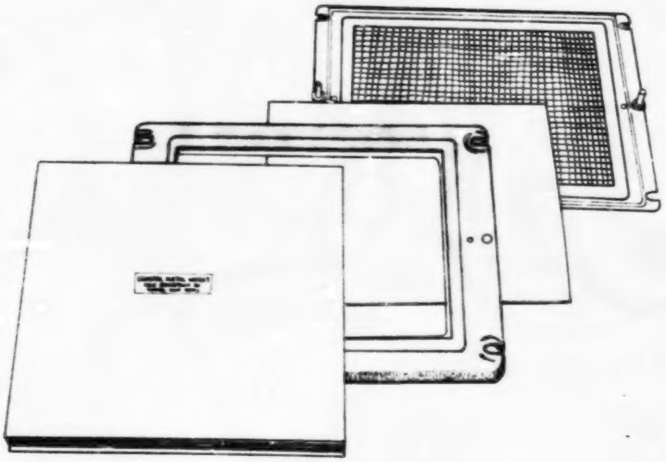

Figure 4-34. Hi-vol cartridge assembly.

When removing the filter, it should be checked for holes or failures and foreign material (such as insects). Caution should be observed to minimize filter damage when removing the faceplate and the gasket. If the border appears fuzzy or non-existent, there may be an air leak around the gasket. The sample should be discarded and the gasket checked. After it has passed the visual test, the filter should be folded in half lengthwise so that sample touches sample. This minimizes sample loss during transport to the lab. If the filter has a nonuniform border, the paper should still be folded so that sample touches sample. Usually the filter is then put into an envelope and a folder and taken to the lab for weighing and analysis. The filter should be put into the conditioning atmosphere for 24 hours before weighing to insure the same humidity and temperature conditions are available for the final weighing as were used for the initial weighing. See Figure 4-35 for a summary of filter-handling procedures.

Documentation of all these steps is important for legal purposes and to ensure data reliability. The operator who starts the sampler is responsible for recording the following information (17).

- Filter number
- Station number and/or address
- Sampler number
- Starting time
- Initial flow rate
- Date and initials
- Summary of conditions that may affect results (e.g., meteorology, construction activities, etc.).

The operator who removes the sample is responsible for recording the following information

- Stop time and elapsed time (if available)
- Final flow rate
- Date and initials
- Summary of existing conditions that may affect results

This documentation is important for calculation of the pollutant concentration in the atmosphere.

Activity	Acceptance limits	Frequency or method of measurement	Action if requirements not met
Filter selection and collection efficiency	1. 0.3 μm diameter particle collection efficiency >99% 2. No pinholes, tears, creases, etc.	1. Manufacturing should furnish proof of DOP test (ASTM-D2986-71) 2. Visually check each filter with aid of light table	1. Reject shipment 2. Return to supplier
Filter identification	Identification number in accordance with specifications	Visually check each filter	Identify properly or discard filter
Filter equilibration	Equilibration in controlled environment for no less than 24 hours. Room: constant humidity chamber employing a saturated chemical solution to afford an RH of less than 50% and constant within ±5%. Average temperature between 20 and 25°C with variation less than ±3%.	For each sample observe: • room or chamber conditions • equilibration period	Repeat equilibration step after 48 hours or more at ambient conditions
Filter weighing	Determine indicated filter weight to nearest milligram within 30 sec. after removal from equilibration environment.	Gravimetric	Reweigh after 48 hours or more at ambient conditions and repeat of equilibration step
Filter handling	Filter in protective folder and envelopes undamaged.	Visually check each filter.	Repack undamaged filters, discard damaged filters.

Figure 4-35. Summary of hi-vol filter handling procedures.

Calibration

Most hi-vol samplers use a rotameter (visi-float), flow recording device, or magnehelic gage for measuring air flow. Since either a fraction of the total sampled air passes through the measuring device or a pressure differential is measured, calibration procedures must be performed against a known air flow. A calibration orifice unit has been designed for these procedures and is pictured in Figure 4-36.

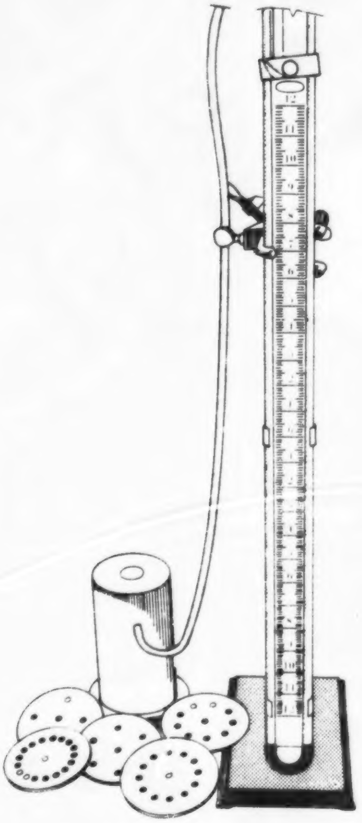

Figure 4-36. Orifice calibration unit. (Courtesy General Metal Works)

This calibration unit consists of a tube 7.6 cm (3 in.) inside diameter and 15.9 cm (6¼ in.) long. A static pressure tap is located 5.1 cm (2 in.) from one end. The end of the tube farthest from the pressure tap is flanged to an outside diameter of about 10.8 cm (4¼ in.). This will accomodate the resistance plates that accompany the calibration unit. The other end of the tube consists of a metal plate over the air inlet with a hole 2.9 cm (1 1/8 in.) in diameter. This hole is the orifice on which the calibration procedures are based. Five resistance plates are provided with the calibration unit representing the resistance of filters with varying particulate loading. The resistance plates have 5, 7, 10, 13, and 18 holes. The plate with 18 holes represents a clean filter; the other plates represent a filter with increasingly heavy dust loading.

To calibrate the orifice unit, a primary standard meter is required. The calibration unit is attached to the inlet of a positive displacement meter (rootsmeter), and a hi-vol motor blower unit is attached to the outlet (see Figure 4-37). A series of steady flows are drawn through the orifice unit for each resistance plate. The air flow is recorded along with the corresponding pressure differential from the manometer attached to the pressure tap of the orifice unit. Placement of the orifice unit before the primary standard reduces the inlet pressure to this meter below atmospheric. To compensate for this, a second manometer is attached to an inlet pressure tap of the primary standard. After recording barometric pressure, the true volume of air drawn through the primary standard is calculated from the following relationship (24).

(Eq. 4-6)

$$V_a = \left(\frac{P_b - P_m}{P_b}\right) V_{meas}$$

Where:

V_a = *true air volume at barometric pressure,* m^3
P_b = *barometric or atmospheric pressure,* mm Hg
P_m = *pressure drop at inlet of the primary standard,* mm Hg
V_{meas} = *volume measured by primary standard,* m^3

Then determine the true air flow rate by:

$$Q = \frac{V}{T}$$

Where:

Q = *true air flow rate* (m^3/min)
V = *true air volume* (m^3)
T = *time of flow* (min)

A plot of the orifice manometer pressure reading (in. of water) versus the true air flow rate is generated (Figure 4-38a). This is used as the calibration curve for this orifice unit. This orifice calibration *should* remain unchanged over a period of time unless the unit is damaged.

Once the orifice unit has been calibrated, it can be used to calibrate high-volume samplers. The orifice unit should be attached to a high-volume motor blower with the 18-hole resistance plate in place. A manometer should have one end connected to the orifice unit with the other end open to the atmosphere. The sampler should be switched on and allowed to run for 5 minutes to set the motor brushes.

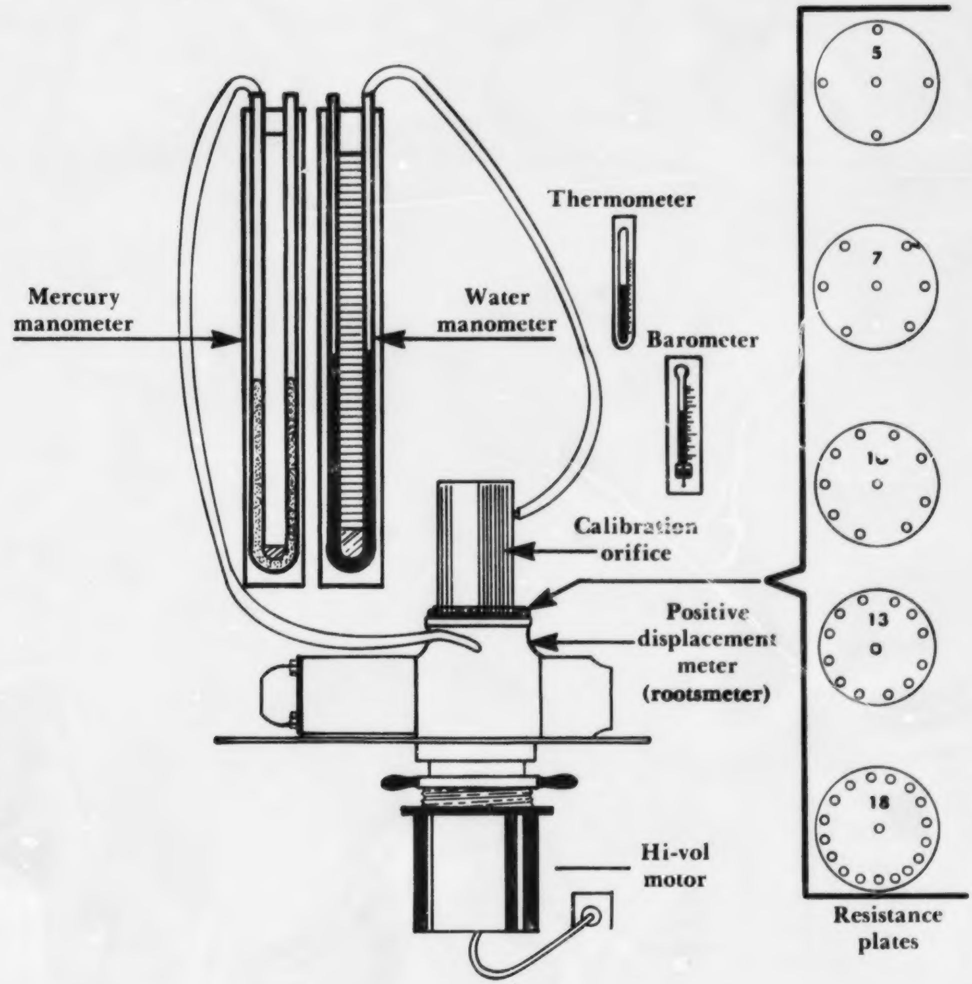
Mercury manometer
Water manometer
Thermometer
Barometer
Calibration orifice
Positive displacement meter (rootsmeter)
Hi-vol motor
5
7
10
13
18
Resistance plates

Figure 4-37. Diagram of orifice calibration set-up.

The reading indicated by the rotameter, continuous recording device, or magnehelic is recorded along with the corresponding orifice manometer pressure value. This is done for all five resistance plates. The orifice manometer pressure value is converted to flow in cubic meters per minute using the orifice calibration curve. A plot of the flow rate versus the rotameter, continuous recorder, or magnehelic reading is plotted and the best fit curve, having not more than one point of inflection, is used as the calibration curve for the high-volume unit (Figure 4-38b).

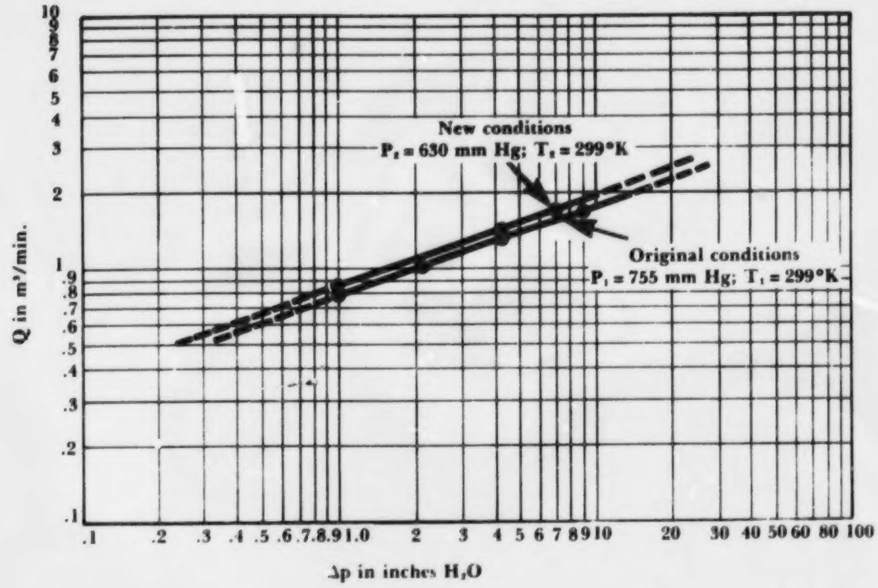

Figure 4-38a. Orifice calibration curve.

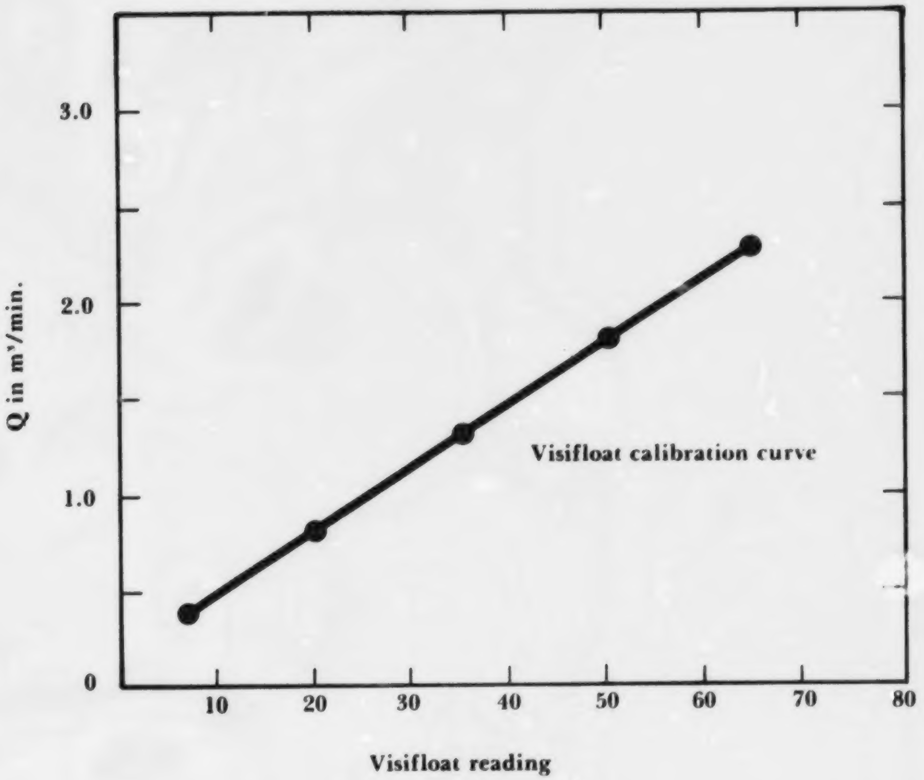

Figure 4-38b. Visifloat calibration curve.

When using an orifice calibration unit to calibrate a hi-vol sampler, corrections must be made to the indicated flow if the actual atmospheric temperature and pressure vary from the calibration conditions*. The corrected flow may be calculated as follows (17):

$$Q_2 = Q_1 \left(\frac{T_2P_1}{T_1P_2}\right)^{1/2}$$

Where
Q_2 = *corrected flow rate*, m^3/min
Q_1 = *uncorrected flow rate, read from orifice calibration curve*, m^3/min
T_1 = *absolute temperature at orifice calibration conditions*, °K
T_2 = *absolute temperature when calibrating the sampler*, °K
P_1 = *barometric pressure at orifice calibration conditions*, mm Hg
P_2 = *barometric pressure when calibrating the sampler*, mm Hg

(Figure 4-38(a) shows new curve drawn to reflect differing conditions of temperature and pressure).

Standard High-Volume Sampling Procedure

The following procedure is recommended for high-volume air sampling

1. Install the sampler in the standard shelter located at a suitable site;
2. Remove the face plate, place a filter in the center of the filter holder and replace the face plate securing it in place by tightening the four wing nuts to equalize the pressure and prevent air leakage;
3. Close the roof of the shelter, turn on the sampler and allow it to run for about 5 minutes; then take a flowmeter reading;
4. At the end of the sampling period (24 hours), take one final flowmeter reading, then stop the sampler. If the sampler has been shut off automatically, turn on the sampler and let it run for 5 minutes to set the brushes before taking an air flow measurement;
5. Carefully remove the filter, fold in half along the longer axis making sure that sample touches sample and place in a protective folder for transportation;
6. Filter number, starting time, ending time, initial and final flowmeter readings, sampler location, and weather conditions should be recorded for each sample collected;
7. Determine the total volume of air sampled by converting flowmeter readings to actual air flows in cubic meters per minute by referring to the sampler calibration curve, then multiplying the average of the initial and final flow rates by the length of the sampling period in minutes; this volume should be corrected to standard EPA conditions.

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*As a guideline, when pressure differs by as much as 15% and temperature (°C) differs by 100% or more from the calibration conditions only a 15% error can be expected. Smith, F., Wohlschlegel, P. S., and Rogers, R. S. C. 1978. Investigation of Flow Rate Calibration Procedures Associated with the High Volume Method for the Determination of Suspended Particulates. EPA report no. 600/4-78-047.

8. Calculate the mass concentrations of suspended particles using the following equations:

(Eq. 4-8)

$$V = \left(\frac{f_f + f_i}{2} \right) t$$

(Eq. 4-9)

$$TSP = \left(\frac{m_f - m_i}{V} \right) \times 10^6$$

Where: TSP = *mass concentration of suspended particulate,* μg/m³
m_i = *initial weight of filter,* g
m_f = *final weight of filter,* g
f_f = *final flow rate,* m³/min
f_i = *initial flow rate,* m³/min
t = *time, min.*
V = *air volume sampled,* m³
10^6 = *conversion of* g *to* μg.

Filters from hi-vol samplers can be analyzed much more thoroughly than is possible from a simple mass concentration determination. After a filter has been weighed, it can be cut into sections for subsequent analysis. Destructive techniques that might be applied are organic solvent extraction, acid extraction, and aqueous extraction.

Atmospheric Organic Analysis

An organic solvent extraction is made with a portion of the filter to determine the amount of organic aerosol present in the ambient air. A solvent such as benzene or chloroform is used in conjunction with a Soxhlet extractor to remove organics from the filter. This organic fraction can be further treated for analysis by infrared or ultraviolet spectrometry.

Atmospheric Metals Analysis

Acid extraction is performed on another segment of the filter paper. The filter can either be placed in an acid bath for several hours or it may be extracted in either a Soxhlet or Bethge apparatus. Several acid mixtures have been suggested for extracting the metals from the filter, yielding solutions of soluble salts. Any filter matter that disintegrates in the acid can be removed by filtration or centrifugation. After further preparation, the soluble metal solution can be analyzed by a number of methods, including atomic absorption spectrophotometry, emission spectroscopy, and polarography.

Water Solubles Analysis

A third portion of the filter is extracted into deionized, distilled water. This extraction will solubilize sulfates, nitrates, and other water-soluble anions and cations. The extracted material is filtered. Water-soluble species can then be analyzed using known methods.

Other Analyses

The filter paper that remains is saved to be used for more nonroutine analyses, or for any other method if it must be repeated because of some error. These other analysis methods might include nondestructive neutron activation analysis, x-ray fluorescence analysis, electron microscopic analysis, etc.

It should be noted that the above-mentioned analysis techniques are not required for all filters. Considerable thought must be used to decide what pollutants should be determined from the filters and what method should be used for subsequent analysis for obtaining the most meaningful results.

Sampling Accuracy and Precision

The limits of accuracy and precision of any sampling method must be understood for proper interpretation of data obtained using that method. Factors influencing the accuracy and precision of high-volume sampling include sampler operating characteristics, accuracy of calibration, filter characteristics, location of sampler, nature and concentration of particulates and gases in air being sampled, and the temperature and humidity of the air.

Accuracy

Accuracy may be defined as the extent to which a measurement agrees with the true value of the quantity measured. In sampling for suspended particulates, there is no standard method for determining true values; consequently, accuracy as defined above cannot be measured. However, there are several situations that are known to lead to inaccurate measurement of suspended particulate concentrations.

When sampling is conducted over a 24-hour period, the final air flow rate is usually lower than the starting flow rate, the difference being greater when the particulate level is high and/or the particulate matter has a strong tendency to plug the filter medium. The change of flow rate with time cannot be predicted and can only be determined by taking air flow readings at intervals throughout the sampling period. Since it would be impractical to take such a series of readings for each sample collected, the currently accepted procedure is to compute the volume of air sampled, by assuming a linear decrease of flow during the sampling period, i.e., multiplying the average of the initial and final flow rates by the length of the sampling period. Air flow measurements obtained by averaging initial and final air flow rates have been compared with those obtained by use of several air flow measurements taken during the sampling period. The results indicate that reasonably accurate flow measurements can be obtained by the use of accurate flow rates. When sampling is conducted in urban areas with high particulate levels, errors of as much as 10% may occur. Fortunately, such incidents are few in number. In urban areas with low particulate levels and in nonurban areas the change in air flow over the normal 24-hour sampling period is relatively small; therefore, the sampling rate is practically constant and the volume of air sampled may be accurately determined.

In some communities inaccurate air flow measurements may result from frequent and sizeable changes in the operating voltage. Use of a constant voltage transformer between the sampler and the power line will ensure against excessive voltage changes.

Modification of the high-volume sampler to permit a continuous recording of air flow during the sampling period provides a more accurate measure of the volume of air sampled. This modification includes the incorporation of a fixed orifice into the motor housing, use of a pressure transducer to monitor the air flow, and a chart recorder to make a continuous recorder of the air flow during the sampling period (Figure 4-39).

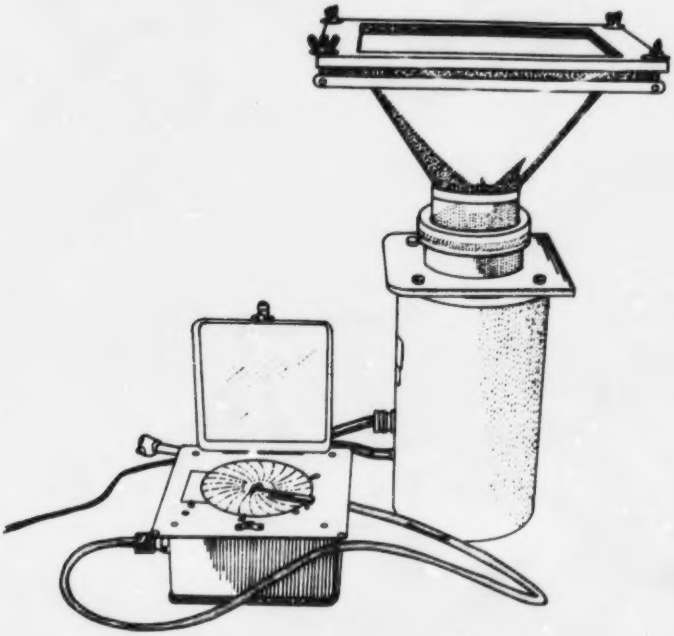

Figure 4-39. Hi-vol setup with flow transducer.

Chahal and Hunter discuss the use of an orifice meter as a more accurate means to measure hi-vol flow rate (see Figure 4-40) (34). Pressure drop across the orifice could be monitored with a pressure transducer for a continuous record of flow. This modification can be performed after the purchase of a hi-vol. If the adapted hi-vol is to be used for Federally required monitoring, permission must be asked for and given for this sampler to be used.

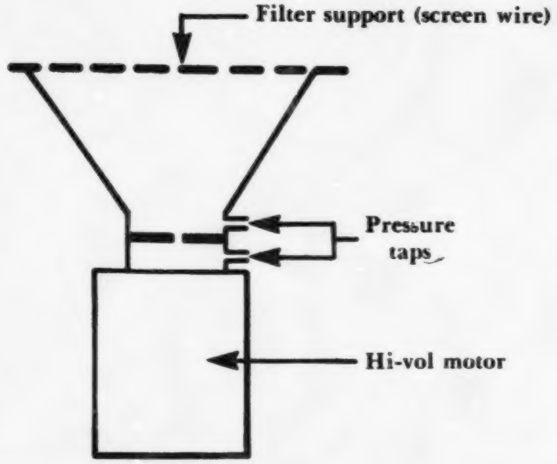

Figure 4-40. Hi-vol sampler with pressure taps.

Non-uniformity in sampling rate is a more serious problem from the standpoint of the representativeness of the sample. To accurately measure the average pollutant level over any sampling period, sampling must be done at a uniform rate. Obviously, a 24-hour sample collected with starting and ending flows of 60 and 40 cfm will not accurately represent the average particulate concentration over the sampling period; the final result will be under- or overestimated, depending on whether the particulate level was higher or lower at the start than at the end. Fortunately, it has been found that, except for in the most heavily populated areas and during prolonged stagnation periods, the drop in air flow rate is minimal and for all practical purposes the sampling rate may be considered essentially uniform for the whole sampling period. However, the largest divergence from uniformity of sampling rate is found in the more heavily polluted areas where accurate information is greatly needed. Non-uniformity of sampling rate and inaccuracies due to nonlinear decrease in air flow can best be eliminated by the use of constant flow samplers, which will be described later.

It has also been shown that the total particulate collection is dependent on the flow rate chosen (9). In a test where identical hi-vols at flow rates between 30 and 60 cfm were tested side by side, the hi-vol running at 60 cfm obtained a particulate value 1% higher than the 50 cfm hi-vol. The 40 cfm hi-vol obtained a value of 3.8% higher than the 60 cfm hi-vol. The 30 cfm hi-vol obtained a value 7.4% higher than the 60 cfm hi-vol. This difference may be attributed to the more efficient trapping of small particles at lower flow rates by glass fiber filters (1).

Other errors associated with hi-vol particulate measurements are:

- Filters have been shown to gain weight during idle or nonsampling periods (35, 36);
- The roof design causes the hi-vol to be wind-direction sensitive;
- Nitrates and sulfates (artifacts) are formed on the filter by reaction (both glass fiber and cellulose) during and after sampling causing erroneously high particulate concentrations (41, 42).

Precision

Precision can be thought of as reproducibility of results obtained by measurements made under the same conditions, at the same time, following identical procedures. The precision of high-volume sampling can be demonstrated by using data collected in a recent investigation of the comparative collection efficiencies of glass fiber filters from two different sources.

Four carefully calibrated and matched high-volume samplers were set up at the corners of an 8-foot square on the roof of a building located in the Mill Creek Valley of Cincinnati. All samplers were started at the same time and had identical initial air flow rates; sampling was terminated at the same time on all samplers. Each day two samplers were fitted with the Gelman Type A filters and two with MSA 1106 BH filters, the samplers being randomly selected each day.

During the study, 40 samples were collected on each of the two types of filters. Average suspended particulate concentration measured was 101 $\mu g/m^3$ with the Gelman filters and 100.5 $\mu g/m^3$ with MSA filters. Thus, one can conclude that the collection efficiencies of the two filters are identical, and, therefore, the study results can also be used to evaluate the precision of high volume sampling. Results for the 20-day period for each of the samplers averaged 97.3, 101.3, 101.9, and 100.7 $\mu g/m^3$ for an overall average of 101.3 $\mu g/m^3$. A careful and detailed statistical analysis of the data showed no significant differences between samplers. This study thus demonstrated the precision of high volume sampling when samplers have been accurately calibrated and properly operated. However, this was a controlled experiment and does not necessarily represent the hi vol precision in actual use.

To insure the quality of data reported from high-volume sampler networks, an accurate, quick, and easy audit technique is needed. One such device, a Reference Flow device (ReF device) has been developed by the National Bureau of Standards under contract to the EPA. This device provides a quick, easy, and accurate technique for flow calibration audits. The ReF device is a modified orifice designed for ease of placement onto a high-volume sampler without dissassembling the sampling unit.

For a more detailed description of the ReF device and audit procedure, see the companion manual to this one, the Laboratory and Exercise Manual for course 435, EPA no. 450/2-80-005, p. 2-27, 2-35.

Constant Flow Samplers and Devices

As mentioned earlier one of the largest errors in hi vol measurements is in the sample flow rate. Combining inaccurate, varying flows with the fact that particulate concentration varies during the sampling period can cause relatively large errors in TSP measurements. Therefore, constant flow through the hi vol sampler should be maintained during the sampling period to ensure accurate TSP measurements. Constant flow control could also facilitate the use of membrane filters to measure heavy metals with the hi vol sampler. The following regulation systems are commercially available to help achieve constant hi vol flow.

Mass Flow Regulation

This method of flow regulation uses a constant temperature thermal anemometer sensor to measure mass flow in the neck of the hi-vol sampling head. Electronic feedback circuitry adjusts the motor speed to maintain a constant mass flow. Since mass flow is controlled, the volumetric flow rate is maintained at standard conditions. Thus, flow variations caused by temperature, pressure, line voltage, and particulate loading are all compensated for by this system. Flow rates can be selected over a wide range allowing the same regulator to be used for standard reference method sampling or for a high-volume cascade impactor. This unit can be retrofitted to any hi-vol.

Pressure Sensitive Regulators

A second type of regulator uses a pressure sensitive switch connected to the exhaust of the sampler to activate a motor-driven variable transformer that controls the speed of the blower motor. Thus, as the sample builds up during sampling, with a corresponding increase in resistance to air flow and lowering of exhaust pressure, the motor speed will be automatically increased to create a higher vacuum and maintain a constant flow rate. Such a device is sensitive and provides a uniform flow. This flow regulator, which operates in the 5 to 50 cfm range, is distributed either as a separate unit or as a component of one constant flow sampler.

Sampling of Respirable Particulates

Samples collected by means of the standard high-volume sample-glass fiber filter combination represent a wide range of particle sizes from 100 micrometers down to those in the submicrometer range. While such samples may be adequate for the definition of total suspended particulate pollution, they are not suitable for the evaluation of potential health effects because only those particles smaller than 10 micrometers are of significance in this respect (Figure 4-41). Various techniques are available for use with the high-volume samplers to permit selective collection of the fraction that is commonly referred to as "respirable particulates" (see Figure 4-27).

A simple technique for respirable particulate sampling, which has not gained wide use, was developed and reported by Roesler (12). This method requires a simple modification of the sampler faceplate to permit the insertion of a ½-inch sheet of 66 ppi polyurethane foam in front of the glass fiber filter, plus the installation of baffles around the perimeter where the air enters the shelter. The polyurethane foam removes practically 100 percent of the larger particles that pass through and smaller (respirable ones) are collected on the filter (Figure 4-42). Using this procedure, a study was made of the relationship between the respirable and total suspended particulates in five cities. The average ratio of respirable to total particulate matter ranged from 0.48 (St. Louis) to 0.586 (Cincinnati) (Figure 4-43). Detailed analyses of samples (Figure 4-44) indicate that by far the greater portion of benzene-soluble organics, sulfates, nitrates, and lead (three of four cities) is found in the respirable fraction. This has gained considerable significance in the investigation of health effects of air pollution.

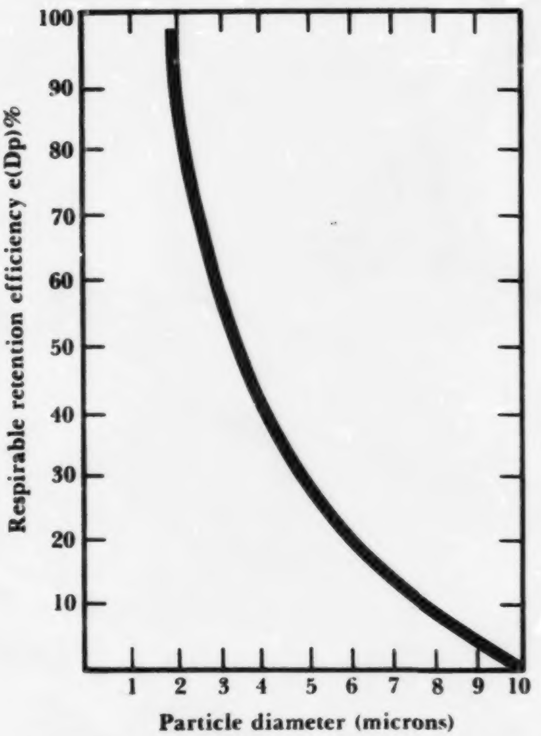

Figure 4-41. Respirable retention vs. particle diameter.

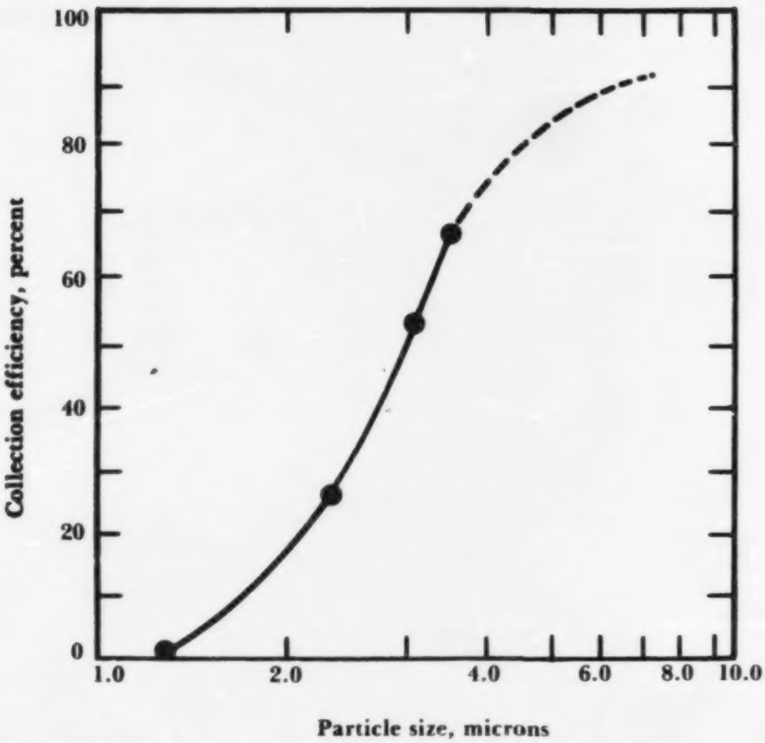

Figure 4-42. Respirable particulate matter curve for a polyurethane foam collector.

City	Minimum	Maximum	Average
Chicago	0.400	0.648	0.494
Philadelphia	0.425	0.924	0.547
Cincinnati	0.542	0.678	0.586
St. Louis	0.375	0.677	0.477
Washington	0.415	0.540	0.490

Figure 4-43. Suspended particulate matter ratios on a concentration basis.

(Ratio = respirable fraction/total collection)

Pollutant	Chicago	Cincinnati	Philadelphia	St. Louis
Benzene-soluble	0.69	0.79	0.77	0.88
Nitrates	0.64	0.62	0.53	0.56
Sulfates	0.84	0.96	0.84	0.87
Iron	0.32	0.41	0.39	0.33
Lead	0.47	0.62	0.69	0.68
Manganese	0.43	0.62	0.50	0.44

Figure 4-44. Respirable/total particulate matter ratios for selected pollutants.

If air is drawn through a properly designed elutriator at a suitable rate, then through a glass fiber filter on a standard high-volume sampler, the larger particles settle out in the elutriator and the smaller ones are collected on the filter. This device permits a rough separation of particulates into the respirable and non respirable fractions but is too cumbersome for use in most situations.

When the high-volume sampler is operated with a cyclone separator of suitable size connected ahead of the filter, a separation into respirable and nonrespirable fractions is accomplished. In this instance, using the proper flow rate and cyclone separator, the particle size distribution of the sample collected on the filter closely resembles that of the particles taken into the human respiratory tract.

A recent study used hi-vols with cyclones that were capable of attaining 50% particle retentions at 3.5, 2.5, 1.5, and 0.5 μm aerodynamic diameters (37). Since the cyclones removed the majority of the particles above these diameters, the hi-vol backup filter could be used as a measure of the particles below the cut points.

Cascade impactors are available for use with high volume samplers. Cascade impactors provide data for a complete size distribution or respirable particles. Two types of high-volume cascade impactors are currently sold. One type uses multiorifice plates with round orifices and operates at 20 ft^3/min while the other type uses multislit plates and operates at 40 ft^3/min. For a complete discussion of high-volume cascade impactors refer to the section in this chapter on "Impaction Devices."

Respirable particulate sampling by the high-volume attachments has shown many disadvantages. Variability in the polyurethane foam made results inconsistent. Errors normally associated with cascade impactors (i.e., particle bounce and shatter, wall losses, etc.) and the inaccessibility of collected particulate for analysis made them undesirable for routine field sampling of respirable particulates. Cyclones and elutriators were too bulky for routine sampling. Because of these and other disadvantages EPA has spent much time and effort developing an acceptable sampler for respirable particulates. A dichotomous sampler was developed and shows great promise as a routine sampler for respirable and total particulates (for a complete discussion of the dichotomous sampler refer to the section in Chapter 4, "Dichotomous Sampler").

Sampling for respirable particulates is already becoming a widely accepted procedure. Once the procedures have been standardized and adopted for routine sampling, the study of the nature of respirable particulates will become an integral part of all State and local sampling programs.

Maintenance

Although the motors used in the Silverman type of high-volume samplers were originally designed for use in household vacuum sweepers, their performance as air sampling devices has far exceeded what one would expect from a component of a household appliance. Modifications to the air mover have made them even more dependable. Naturally, brush and motor life have been considerably shortened due to the excessive demands of air sampling for longer continuous operation of the sampler. Brushes wear out and have to be replaced at frequent intervals, and new motors must be installed when brush wear becomes excessive. Motor and brush life can be extended substantially without seriously decreasing the amount of sample collected if the sampler is operated at a slightly reduced voltage by use of a "Buck or Boost" transformer. Many constant flow manufacturers claim increased brush life because the voltage is "bucked" by the controller. Occasional cleaning and/or replacement of the flowmeter, flowmeter tubing, and face plate gasket, and replacement of the rubber gasket between the motor and sampling head, complete the maintenance requirements.

Application of High-Volume Sampling

Samples and data obtained by high-volume air sampling may serve many purposes, several of which are discussed below.

Nature and Magnitude

The operation of high-volume samplers at strategic locations in a community will result in the collection of samples collectively representing the particulate pollution of the community. Quantitative analysis of the samples provides information on the ambient concentrations of the various pollutants. Figure 4-45 (22) illustrates the type of data obtained, which helps to define the nature and magnitude of particulate pollution. Such information also provides clues as to the existence of potential health hazards.

	Urban[a]		Rural[b]	
Average conc	Fine 29 $\mu g/m^3$	Coarse 22 $\mu g/m^3$	Fine 26 $\mu g/m^3$	Coarse 15 $\mu g/m^3$
Si	1.00%	8.00%	0.50%	4.00%
S	12.50	1.40	12.60	0.90
K	0.40	1.20	0.30	0.90
Ca	0.70	8.20	0.50	4.20
Ti	1.10	2.00	$<$ 0.10	0.20
Fe	1.40	4.80	0.30	1.30
Zn	0.35	0.20	0.13	0.15
Br	0.33	0.16	0.06	0.04
Pb	2.20	0.60	0.51	0.11

[a] Located at the Missouri Botanical Garden in St. Louis.
[b] Located in an agricultural area in Illinois, 40 km south of St. Louis.
Fine = particles less than 3.5 microns in diameter.
Coarse = particles greater than 3.5 microns in diameter.

Figure 4-45. Mass and percentage composition of size-fractionated St. Louis aerosol samples from August 18 to September 7, 1975.

Trends

Data obtained in a high-volume sampling program of many years duration may be used to predict trends and the air pollution levels in a community. Detection of trends by the examination of data on a sample basis is difficult due to the wide ranges of values; however, application of sophisticated statistical smoothing techniques offers a solution to this problem (18). Seasonal trends may be detected by limited smoothing (Figure 4-46), whereas more drastic treatment is required to demonstrate long range trends (Figure 4-47). Likewise, a properly designed sampling program may be used to monitor the effectiveness of an air pollution control program. The same statistical treatment of the data serves this purpose also. Yearly trends for national air quality and emissions are published by the Office of Air Quality Planning and Standards of the Environmental Protection Agency.

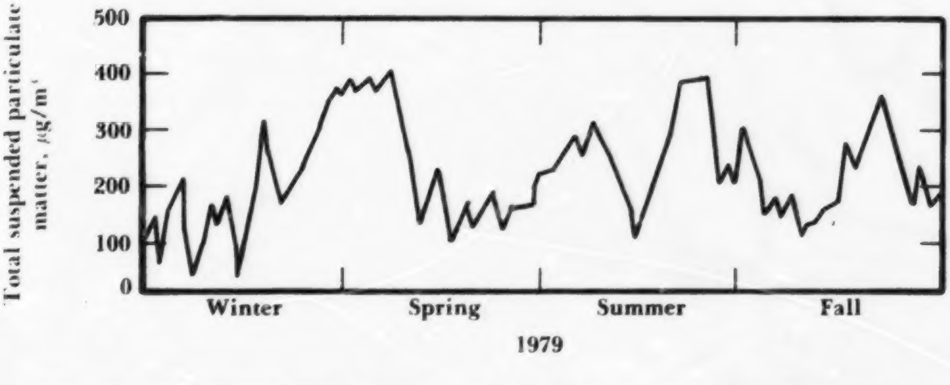

Figure 4-46. Seasonal trends in concentrations of suspended particulate matter.

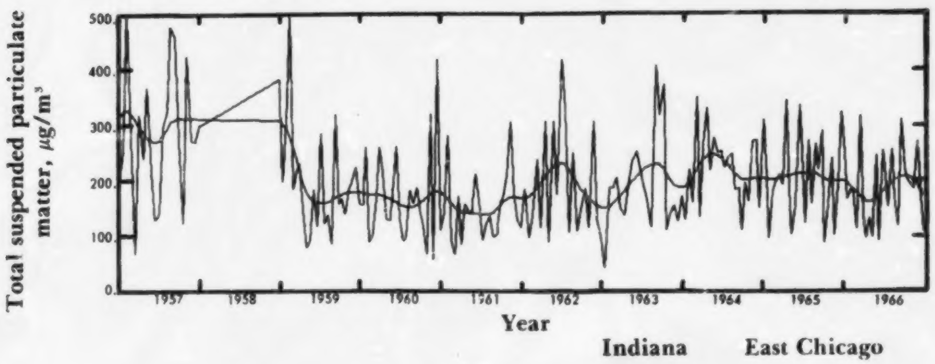

Figure 4-47. Long range trends in concentrations of suspended particulate matter. (Data obtained in East Chicago, Indiana)

Air Quality Standards

Data of the type shown in Figure 4-45, used in conjunction with recognized criteria, may serve as a basis for the establishment of community air quality standards. It would be impossible to set realistic standards without an accurate picture of existing ambient air quality. If the existing air quality is accurately known, realistic standards can be set on the basis of the degree of control of emissions required to meet these standards.

Source Contributions

High volume air sampling can be used to evaluate the contribution of pollution to the atmosphere from a specific source. Two samplers controlled by a wind direction indicator are required. One sampler operates only when the wind comes from the direction of the source in question; the second operates only when the wind is from the other directions. The difference in the particulate concentrations of the two samples represents the mass contributed by the source. A chemical analysis will characterize the nature of pollutants from the particular source.

Health Effects

Detailed studies of the chemical nature and biological activity of the benzene-soluble organic fraction of suspended particulate matter require several hundred milligrams of material. This has been supplied by pooling the benzene extracts of hundreds of individual samples obtained in the routine analysis of network samples or by operating several high-volume samplers continuously for more than a year to provide the large amounts of experimental materials required. Much of the fundamental research on chemical and biological detection and measurement of carcinogens was done on samples obtained by means of the high-volume sampler, flash-fired glass fiber filter system of air sampling (2, 3, 5, 14, 38, 39). More recent work has required kilogram quantities of organic materials, which have been obtained by extracting low-blank used filters from the ventilating systems of large office buildings.

The hi-vol can be used for the above purposes but it inherently lacks the ability to provide continuous data on particulate concentration. Nephelometry, one of the more acceptable methods that gives a continuous particulate concentration, uses the light scattering properties of aerosols. Kretzschmar (40) found that nephelometers correlated well with TSP measurements made by the reference hi-vol method. Further work is needed to develop a sampler that accurately measures particulate concentration on a "real-time" basis.

Summary

The high-volume sampler has become the most widely used tool for monitoring particulate air pollution. It is a low cost, portable, easily maintained, and reasonably precise sampling device. Improvements in sampler performance have resulted from incorporation of automatic timers, flow rate recorders, constant flow devices, and size separation devices, into the basic system. Although hi-vols have been the accepted standard in particulate monitoring several needs remain to be filled. One need is for a sampler that separates respirable and nonrespirable particles for gravimetric and chemical analysis. The dichotomous sampler may replace the hi-vol for these particulate measurements. Another need is for instrumentation that provides "real-time" particulate measurements.

Sample Problem

Determine the particle mass concentration from the following filter and flow rate data.

Mass of Filter:	
Before	3.182 g
After	3.455 g
Flow Rate:	
Start	1.70 m^3/min
Finish	1.41 m^3/min
Time:	
Start	Midnight 8/11/71
Finish	Midnight 8/12/71

Solution:

$$\textit{Average Sampling Rate} = \frac{1.70 + 1.41}{2} = 1.555\ m^3/min$$

$$\textit{Sampling Volume} = \frac{1.555\ m^3}{min.}(24\ hr.)(60\ min./hr.) = 2239.2\ m^3$$

$$\textit{Mass of Collected Material} = 3.455 - 3.182 = 0.273\ g$$

$$\textit{Concentration} = \frac{0.273\ gm}{2239.2\ m^3}\ 121.9 \times 10^{-6}\ g/m^3 \times 10^6\ \frac{\mu g}{g}$$

$$\textit{Particulate Concentration} = 122\ \mu g/m^3$$

Questions

1. A high volume filter weighed 2.1600 grams before sampling. The filter was installed at midnight on 12-25-77. The initial flow rate was 1.50 m^3/min. and the final flow was 1.32 m^3/min. The sampler was shut down at midnight on 12-26-78. The filter weighed 2.4508 grams after sampling. What was the TSP concentration? (Ans.: 113 µg/m^3)
2. Why is it necessary to sample for respirable particulates?
3. Give several reasons why constant flow regulation of high volume samplers is necessary.
4. Particulate concentrations by the high volume method have recently been doubted because of several sampling errors. What are some of these errors?

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Evaluation of Filter Media

Introduction

There has been a tremendous increase in the use of filter media for collecting airborne particulate matter; in the fields of air pollution and environmental radiation surveillance, it is the primary means of particulate sampling. Many circumstances have contributed to this situation, among which are the low cost and simplicity of filter sampling. Topics to be discussed in this section include the basic advantages and disadvantages of air sampling with filters, filtration theory, and some of the criteria necessary for the selection of a filter media to be used in a specific sampling program. Although the term filter media can be extended to cover a large number of media, such as filter thimbles and granular beds, this discussion will be confined to the more common media available in sheet form commonly referred to as filter papers.

General Considerations

Advantages

There are several advantages of filter sampling for particulates over other methods. A primary one is the feasibility of handling large volume rates of flow. Some dust sampling instruments, such as midget impingers and thermal precipitators, do not have this capability for large flowrates. Also, after collection, the filtered sample is usually readily available for direct observation.

The number of sizes of filters available has proved to be another advantage. By changing the size of the paper, the volume of air sampled can be varied while still maintaining the same linear flowrate through the filter. The selection of sizes also allows filter holders to be designed for use in a variety of situations. This is a definite advantage when the sampling space confines limit accessibility. The variability among filters extends beyond the matter of size alone. Appropriate filters can be obtained that are capable of sampling over a wide range of environmental conditions of temperature, humidity, and dust loadings. Further, filters can be found that are adaptable to analysis schemes ranging from microscopic examination to elaborate chemical separation schemes.

Disadvantages

The use of filter media for sampling is not without its difficulties, one of which is related to the variation in physical and chemical properties among a quantity of any given filter papers. In the case of an impaction instrument, once its operating characteristics have been determined these should remain relatively fixed. On the other hand, in sampling with filters, the paper is changed between each sample collection. Although filters can be obtained that minimize the variability between individual filters of a specific type, it is more common to find significant differences in performance, particularly between different lots of filters. Smith and Nelson (13) have prepared guidelines for a quality assurance program, which, if followed, will enable the user to control the effects on sampling and analysis resulting from inconsistencies between filters.

Another case in which filters are at a disadvantage is in conjunction with selective particle sizing. A cascade impactor can, theoretically, be designed so that particles of different size ranges can be collected on different stages of the impactor. Such a size separation can hardly be done with filter media, although some gradations are possible (17).

The Theory of Filtration

The most common misconception about air filtration is that it is primarily a sieving mechanism. If this were the case, only particles larger than the pore size would be trapped and the theory of collection would be relatively simple. Actually, outside of the kitchen strainer, very few media could be classified as pure mechanical strainers. In air filtration a number of mechanisms contribute to the collection of particulates. The degree to which each one contributes is a function of a number of parameters, discussed below. For a more complete discussion of filtration theory see R. D. Cadle's book on *The Measurement of Airborne Particulates* (Wiley Interscience, 1975).

Diffusion

The collection of particulates on a filter by diffusion depends on a particle concentration gradient between the filter and the air passing between the fibers. The highly concentrated particles in the air stream diffuse to the filter fiber where the concentration is near zero. The diffusion theory further postulates that when the particle comes in contact with the filter it remains there. The contribution made by diffusion depends on the transit time of particles through the filter, with a longer time resulting in greater diffusion contribution. The amount of diffusion will then depend on linear rate of flow, filter thickness, size of particle, interfiber distance, and particle concentration in the air. The effect of diffusion increases as particle size approaches molecular dimensions.

Direct Interception

Direct interception can be considered as that part of the filter collection mechanism that is analogous to mechanical straining. The interception mechanism takes place when a particle following its air movement streamline comes within a distance from the filter material which is equal to, or less than, the particle radius so that it comes in contact with the filter medium. As with simple straining, this type of collection predominates where the particles are greater in diameter than the interfiber distance, or pore size. The effectiveness of direct interception increases with increasing particle size.

Inertial Collection

As a particle is carried by an air stream it possesses a certain amount of inertia, depending on its mass and velocity. When a sufficient inertial force has been established, the particle will, as the air stream turns, leave its streamline and continue on its previous path. If the inertia of a particle causes it to strike a filter fiber during the passage of the air stream around the fiber, the particle will be collected. The mechanism of inertial collection plays a major part where high linear velocities of airflow are present. Increasing the particle size and decreasing the fiber diameter (or pore diameter) improves the effect of inertial collection.

Electrical Forces

If the aerosol particle has an electrical charge, and the filter fiber has a charge of opposite sign, the particle will be attracted to the filter media. Many investigators feel that such a mechanism has a part to play in the filter sampling of air. Experiments (5) have indicated that both atmospheric particles and filter media possess electrical charges and that collection does occur by this means. The magnitude of the effect is not well known, but it probably is a definite contribution to the process of collecting particles smaller than the pore size.

Combined Factors

During actual filtration all of the above-mentioned collection mechanisms are working together so that it is often difficult to separate one from another. Furthermore, other mechanisms occur that complicate the situation. All of the methods of collection th~~at hav~~e been discussed postulate that once a particle touches the filter material it stays there. This is not entirely so there is some reentrainment of particles resulting from the airflow through the filter picking up and carrying material that has been previously deposited some distance before the particles are once more entrapped by the filter fibers. Increasing the filter face velocity will increase the chances of reentrainment.

Collection Efficiency of Filters

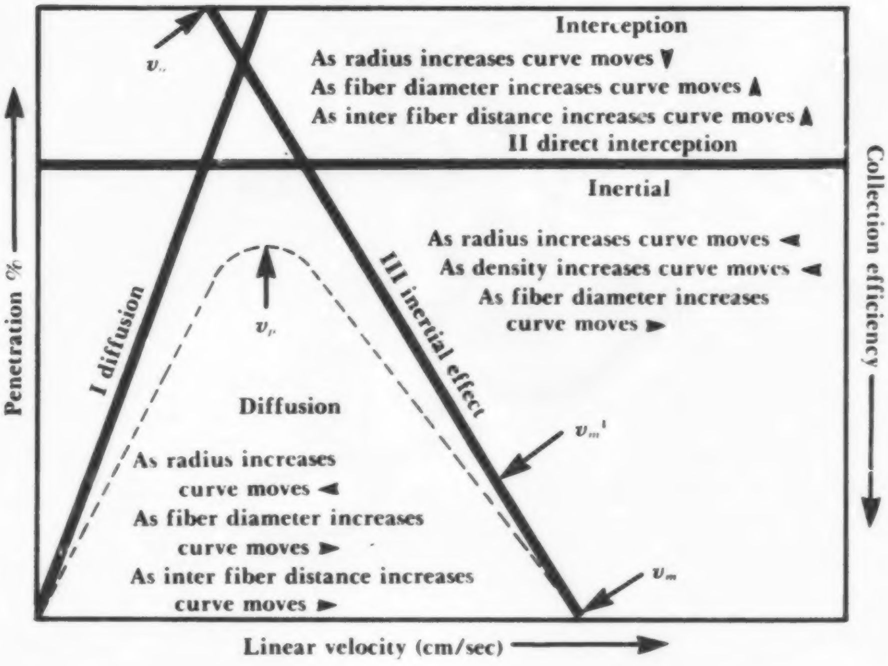
In any procedure where an attempt is made to relate a sample activity to an activity concentration in the environment, the volume of original sample must be known. In the sampling of air particulates by filtration, not all particles in the air are collected. That is to say, the collection mechanisms that have been discussed are not 100% efficient. It is, therefore, not sufficient just to know what volume of air was passed through the filter, the fraction of the airborne particles collected must also be known. Collection efficiency may be stated in terms of several parameters. The most common is to determine the *percent penetration* (percent passing through the filter) of a certain particle size as a function of the linear velocity (volume rate of flow divided by the filter area) through the filter. Another way of presenting the efficiency would be to have *percent collection* of a certain particle size as a function of linear velocity through the filter. Although efficiencies of this type are useful, it would be most difficult to use them to determine the fraction of the atmospheric particulates collected unless the particle size distribution existing in the atmosphere were known.

A further complication arises in the determination of airborne radioactivity because, in order to evaluate what fraction of the radioactive particulates have been sampled, a knowledge of the *size distribution of radioactive particulates* in the atmosphere should be known. This difficulty has great significance if an attempt is to be made to relate the analysis to health significance, as the radioactive particle size versus lung retention should be evaluated. In practice many simplifying assumptions are made. One method is to assume a minimum collection efficiency for all particle sizes, and further assume that the radioactive particles are all of this minimum collectable size. It is admitted that these are greatly simplified assumptions, but from the standpoint of health significance, they are also on the safe side.

There is one other type of filter collection efficiency that is reported in the literature. This is a *mass collection efficiency* based entirely on the percentage of the mass of the airborne particulates that are collected. This can be grossly misleading, as the small particles predominate in number, and yet, constitute a minor fraction of the total particulate mass. The only time a mass collection efficiency would represent a total particle collection efficiency would be if all the particles were of the same size.

Theory of Collection Efficiency

Before continuing the discussion of collection efficiency, it is necessary to discuss the theory of collection efficiency for the various collection mechanisms previously mentioned, and also, the effect of various parameters on collection. Figure 4-48 shows a qualitative picture of the theoretical percent penetration versus linear velocity that might be expected for a given filter and an aerosol with a specific size particle. By referring to this graph, and the associated notes, the interrelation of the various mechanisms can be examined.



Interception
As radius increases curve moves ▼
As fiber diameter increases curve moves ▲
As inter fiber distance increases curve moves ▲
II direct interception
Inertial
As radius increases curve moves ◄
As density increases curve moves ◄
As fiber diameter increases curve moves ►
v_a
v_p
I diffusion
III inertial effect
Diffusion
As radius increases curve moves ◄
As fiber diameter increases curve moves ►
As inter fiber distance increases curve moves ►
$v_m{}^1$
v_m
Penetration % →
Collection efficiency →
Linear velocity (cm/sec) →

Figure 4-48. Filtration mechanisms.

Diffusion Efficiency

The diffusion line (I) of Figure 4-48 shows how the diffusion mechanism is affected by linear velocity. As the velocity increases, the diffusion mechanism decreases. As previously mentioned, this is due to the shorter transit time through the filter at the higher flow rates. The diffusion function always passes through the origin but the slope varies with the particle radius, the filter fiber diameter, and the distance between filter fibers.

As the particle radius increases, the slope becomes greater, thus resulting in a reduced diffusion effect for a given linear velocity. This is because larger particles are not as readily affected by diffusion mechanisms as smaller particles.

The effects of fiber diameter and interfiber distance are quite similar. As either of these two parameters increase, the influence of the diffusional mechanism increases, and the slope of the line decreases. A greater fiber diameter increases the diffusion effect, because for a given linear velocity the particle spends a longer time passing by a filter fiber. The effect of interfiber distance is similar as it too affects the transit time of the particle by a filter fiber. The larger the interfiber distance the greater is the open space in the filter; therefore, for a given overall linear velocity, the velocity in the open space of the filter is less for larger interfiber distance, and transit time is longer.

Direct Interception Efficiency

As previously mentioned, direct interception is analgous to simple mechanical straining. As shown in line II of Figure 4-48, there would not be any effect of changing linear velocity on this collection mechanism.

The effects of the particle radius and interfiber distance on the interception mechanism are quite simple. As the particle radius increases, the percent penetration decreases, as would be expected for straining. As interfiber distance increases, the percent penetration increases for a given size, again, as would be expected from mechanical straining.

The relation between particle penetration and fiber diameter for interception is somewhat more involved. As the fiber diameter increases in size, the air flowlines are affected at an increasing distance upstream from the fiber. This may cause some of the flowlines to diverge from a path that would have brought the particle within contact distance of the fiber. Therefore, as the fiber diameter increases, the collection efficiency due to interception decreases.

Inertial Effect Efficiency

The inertial collection of particles depends on the particles leaving their air flowlines and contacting a filter fiber due to their inertial forces. For a particle of a given size, this effect would start to show at some velocity, v_o, and would reach a maximum at some greater velocity, v_m. The fact that the effect increases with velocity is due to the dependence of inertial forces on both mass and velocity. Although Figure 4-48, line III shows a zero percent penetration for this mechanism at v_m the penetration might be significant, depending on the interfiber distance. If a larger interfiber distance existed, the maximum effect might occur at some point v'_m; in which case, a definite amount of penetration would occur.

The effect of increasing particle radius in inertial collection is improved collection for a given linear velocity. This is related to the fact that the larger the particle, the greater is the probability of it coming within a distance from the filter fiber where it will make contact. Figure 4-57 lists the collection efficiency of some filter media as a function of particle size.

The effect of increasing particle density also improves inertial collection. Like the effect of velocity, this is due to the increasing of inertial forces, thus causing greater deviation from the air flowlines.

As the filter fiber diameter increases, the effect of inertial collection decreases. With the air flowlines being affected at a greater distance upstream from the fiber, the change in their trajectory is much more gradual and, therefore, the tendency of inertial forces to cause a particle to leave a flowline is less.

Overall Efficiency

In filter sampling all of the collection mechanisms are taking place simultaneously and their effects are algebraically additive. The overall relation between percent penetration and linear velocity might well look like the dotted line in Figure 4-48.

From this overall efficiency curve, it is seen that there appears to be some velocity, v_p, where a maximum penetration occurs and this has been confirmed in several investigations (4, 9, 12, 14, 15, 18). It should be pointed out, however, that if the direct interception effect is dominant enough, the overall efficiency curve may well have a flat plateau rather than a single velocity of maximum penetration.

The mechanism of electrical forces has not been covered in this discussion of the theory of collection efficiency. The degree to which it will change the overall efficiency is dependent on many factors. The theoretical aspect of this effect is beyond the scope of this discussion, but the fact that it may well play an important part in certain instances is not to be ignored (2, 5, 8).

Experimental Collection Efficiencies

Many investigators have studied the actual collection efficiencies of filter media and their results are reported in the literature (2, 3, 5, 9, 12, 13, 14, 18, 22). A degree of caution must be exercised in utilizing this experimental data. A number of different types of particulates have been used, including dioctyl phthalate (DOP) smoke, atmospheric dust, duraluminum dust, radon daughter products, polystyrene aerosols, and lead fumes. The experimental results of the various investigators often appear to be in great disagreement for many of the filter media, and these differences should be evaluated in selecting an efficiency value to use.

One additional complication factor should be mentioned in relation to filter efficiency. During the time that the sampler is running, the increasing amount of particulates that accumulate on the filter will cause the collection efficiency to improve as sampling continues. At the same time, however, the resistance of the filter to airflow also increases, thus perhaps interfering with the sampling procedure and decreasing the flowrate.

Characteristics of Filter Media

A great number of individual types of filter papers are available. In general, they fall into four main categories: cellulose fiber, glass fiber, mixed fiber and membrane filters. These various categories will be discussed in terms of their general characteristics, sampling considerations, and analysis considerations.

Cellulose Fiber Filters

The filter papers in this category are typically called chemical filters. They were designed for use in "wet" chemistry where liquid-solid separations were desired. Although not designed with air sampling in mind, a number of these filters have seen extensive application in this area (see Figure 4-49).

Filter	Void size microns	Fiber diameter microns	Thickness microns	Weight per unit area mg/cm²	Ash content %	Maximum operating temp. °C	Tensile strength	Flow resistance 100 ft/min in H_2O
Whatman 1	2 +	—	130	8.7	0.06	150	1.67 kg/cm	40.5
4	4 +	—	180	9.2	0.06	150		11.5
32	1 –		150	10.0	0.025	150		38 (lfm)
40	2		150	9.5	0.01	150		54
41	4 +		180	9.1	0.01	150	1.41 kg/cm	8.1
42	>1		180	10.0	0.01	150		46 (28 lfm)
44	>1		150	8.0	0.01	150		40 (28 lfm)
50	1		100	10.0	0.025	150		49 (28 lfm)
541	4 +		130	8.2	0.008	150	2.24 kg/cm	
S&S 604			200		0.03	80		8.5
MSA Type S			100.0		1.5	120		6.5
Cellulose			1000		1.3	120		
Corrugated Cellulose			1000		1.3	120		
MSA BM 2133			1830	32.7	0.12		0.58 kg/cm	9.1
IPC 1478	—	Av.17	560-760	14.6	0.04	120	0.18 kg/cm	0.31
Gelman W-41	24							

Figure 4-49. Cellulose fiber filters.

Sampling Considerations

Cellulose fiber filters are made of purified cellulose pulp, thus rendering them ineffective at high operating temperatures. The low ash content of these filters make them highly suitable to analysis where heat or chemical ashing is a required preparation. These filters generally have a high affinity for moisture. This limitation means that the relative humidity must be controlled while weighing the filters to ensure there is no error introduced by absorbed moisture. Recent studies show that cellulose filters irreversibly absorb water, thus a control blank is required when humidity is a problem. Cellulose filters also enhance the artifact formation of sulfate and nitrate.

Specific Filters

Whatman 41 filter paper is the most widely used of the cellulose fiber filters. Whatman 41 has become the preferred substitute to glass fiber filters for high volume sampling because of the good collection efficiency and acceptability for further chemical analyses. It has also received wide use in all metals analysis including neutron activation analysis because of the low blanks (see Figure 4-58). This filter has also found applications as the tape used with paper tape samplers for the determination of soiling index.

The MSA type "S" filter is well adapted to high-volume sampling because of the low pressure drop. This filter is difficult to handle because of its bulkiness and its variable ash content and organic binder make it unsuitable for some chemical analyses.

TFA filters have also been used for high-volume sampling when extensive chemical analysis is required. Whatman 41 is preferred over this filter because of the higher collection efficiency (see Figure 4-57).

Glass Fiber Filters

These filter papers are made from finely-spun glass fiber by combining the fiber with an organic binder and compressing this material in a paper machine. These filters have seen increasing use in air sampling.

Sampling Considerations

These filters have the ability to withstand high temperatures (up to 540°C), thus making them most attractive for stack sampling. They are further typified by high collection efficiency. In some cases, the organic binder may interfere with subsequent analysis, so the filter is flash-fired to remove the binder material. This causes some loss in tensile strength and usually requires that a backing material be used during sampling. The glass filters are nonhydroscopic, thus allowing them to be used in areas where humidity is high. Being glass also makes them the filter choice for most corrosive atmospheres. All of the filters in this category are quite fragile and must be handled with care.

Analysis Considerations

Glass fiber filters, because of the high silicate content, are extremely difficult to ash by chemicals or heat. Therefore, extraction procedures are performed on these filters to remove the sample for subsequent chemical analysis. For this reason flash-fired glass filters are major atmospheric sampling filters.

The pH of the filter will effect the collection of the sample. It has been recommended (13) that neutral pH ($6.5 < pH < 7.5$) filters be used because there is less absorption of acid gases onto the filter. Significantly different results can be obtained when sampling side by side with filters of different pH values (Figure 4-55).

Specific Filter

The MSA 1106 BH is one of the flash-fired glass fiber filters, and, therefore, free of organic binder. Special mention should be made of the Gelman Spectro Grade Type A Glass Fiber Filter. This neutral pH glass fiber filter has been rated as ultra pure for metals analysis to minimize interference with trace metal background values. (Each box of 8" × 10" filters contains assay information on trace metals for the enclosed filters.) Spectro grade filters do not absorb detectable amounts of SO_2 from the atmosphere, thereby minimizing its effect. A summary of the physical characteristics of glass fiber filters is given in Figure 4-50.

Filter	Void size microns	Fiber diameter microns	Thickness microns	Weight per unit area mg/cm²	Ash content %	Maximum operating temp. °C	Tensile strength	Flow resistance 100 ft/min in H_2O	Benzene extract/100 in² mg
MSA 1106B*			180-270	6.1	~ 95	540	3.5 lb in	19.8	17.3
1106BH#			180-460	5.8	~ 100	540	1.5 lb in	19.8	0.6
Gelman A#			380	9.3	99.4	480		18.9	0.6
E*			380	10.0	98.1	480		18.9	
G			810	11.6		480		3.0	
M			580	10.8		480		6.1	
H			510	12.7		480		21.7	
Whatman									
AGF A#	>1		340	5.3	100	540	1.29 lb in		0.8
AGF B#	>1		840	15.0	100	540	3.14 lb in		3.2
AGF D	>1		460	5.5	100	540	.56 lb in	2.3@2 lfm	
AGF F	>1		380	6.3	100	540	.73 lb in		
H&V H-93		0.6	460-560	9.3	96-99	540	2.5 lb in		
H-94		0.5-3	380	8.2	96-99	480	2.5 lb in		
S&S 24*									
26#			200	6.05					0.3
27*			125-180		98	400			
29#			127	5.4	98	400			0.6

#without organic binder
*with organic binder

Figure 4-50. Glass fiber filter characteristics.

Mixed Fiber Filters

Not too much can be said of this category except that they possess the characteristics of the individual fibers composing them. The chemical analysis of mixed fiber filters also depends on the individual fiber constituents. General characteristics of a number of the members of this category are given in Figure 4-51.

Filter designation	Composition	Void size microns	Fiber diameter microns	Thickness microns	Weight per unit area mg/cm²	Ash content %	Maximum operating temp. °C	Tensile strength	Flow resistance at 100 ft/min (~50 cm/sec) in H_2O
H&V H-70, 9 mil	Cellulose asbestos		0.1–35	230	8.2	20–25	150	2.5 lb/in	17
H-70, 18 mil	Cellulose asbestos		0.1–35	460	15.4	20–25	150	4.0 lb/in	26
H-64	Cellulose asbestos		0.1–35	830-1090	22.7	15–20	150	2.0 lb/in	15
H-90	Cellulose glass		9–35	685	13.4	70	150	3.2 lb/in	0.4
H-91	Cellulose glass		1.5–35	710	13.5	80	150	3.5 lb/in	0.89
N-15	Synthetic fiber & glass		0.5–15	1270	24.9	15	150	1.0 lb/in	9.9
5-G	Synthetic fiber glass & cotton		0.5–15	685	14.5	4–6	150	gauze backed	2.0
MSA glass & cellulose	Glass & cellulose			1000			120		
Whatman ACG-A	Glass & cellulose	> 1		330	5.5		150	270 gm/cm	0.9 (20 lfm)
ACG-B	Glass & cellulose	> 1		990	19.5		150	330 gm/cm	2.6 (20 lfm)
H&V CWS-6	Cellulose asbestos			762		11%			17
H&V AEC-1	Cellulose asbestos			762		13%			13.3
VM 100 Gelman	Vinyl metracel	10.0							
VM-1	Vinyl metracel	5.0							

Figure 4-51. Mixed fiber filter characteristics.

Membrane Filters

This filter media consists of dry gels of cellulose esters, usually produced as cellulose acetate or cellulose nitrate, polyvinyl chloride, acrylonitrile, and Teflon®. The filters are cast on a smooth flat substrate and exposed to a controlled atmosphere. The process can control both the internal membrane structure and pore size (8). Some filters are formed with pores while others are formed as sheets with pores formed later.

Sampling Considerations

Membrane filters are typically very brittle and require careful handling. In air sampling they should be backed by some support structure to avoid breakage. The filters are not too well suited to stack sampling, as they have an operating temperature range comparable to cellulose fiber filters (see Figure 4-52).

The particle sizes collected by membrane filters have been found to be much smaller than the pore size; this is thought to be due to electrostatic forces.

A comparison can be made between the filters supplied by two major manufacturers, Millipore and Gelman. The Millipore filters have a different texture on the two sides created in the manufacturing process. Lindeken et. al. (7) report that Millipore filters with nominal pore diameters less than one micron have smaller openings on the top side than on the bottom. For Millipores with nominal pore sizes above one micron, this situation is reversed. It is the top side pore opening that is reported as the nominal size, and Millipore filters are packed with this side up. The one exception to this is Millipore SM, which is packed with its nominal pore side down. The Gelman filters have approximately the same pore size on both sides. This consideration becomes important when sampling for alpha radioactivity as the small side of the Millipore would be the preferred upstream side in order to minimize the depth that particles go into the filter. Because of these differences in the two makes of filters, the Gelman filters have a smaller pressure drop at equivalent pore diameters. Both filters have appreciable pressure drops, however, and this may limit the volume of air that can be sampled. Another factor limiting the volume of air that can be sampled is the build-up of a second layer of dust on the filter surface. This layer has a tendency to slough off, causing loss of part of the sample.

Filter	Pore size microns	Index refraction	Thickness microns	Weight per unit area mg/cm²	Ash content %	Maximum operating temp. °C	Tensile strength	Flow resistance 100 ft/min in H_2O
Millipore SM	5.0	1.495	170	3.6	0.0001	125	100 psi	19
SS	3.0	1.495	170	3.8	0.0001	125	150 psi	38
WS	3.0		150	4.9	"	"		~100
RA	1.2	1.512	150	4.2	"	"	300 psi	62
AA	0.80	1.510	150	4.7	"	"	350 psi	91 (39)*
DA	0.67	1.510	150	4.8	"	"	400 psi	120
HA	0.45	1.510	150	4.9	"	"	450 psi	210
WH	0.45		150	5.7	0.0001	"		~270
Gelman AM-1	5.0		200	3.6		"	.41 kg/cm²	11
AM-3	2.0		200	6.6		"	.72 kg/cm²	33
AM-4	0.65		200			"		73
AM-5	0.65		200			"		
AM-6	0.40		200	5.8		"		
S&S AF-600	7.5		180-250	6.3-8.7	0.01	Continuous 100		
AF-400	1.0		180-250	6.3-8.7	0.01	Peak 200		
AF-250	2.0		160-210	5.6-7.3	0.008	"		
AF-150	0.85		160-210	5.6-7.3	0.008	"		
AF-100	0.70		Av 150	Av 5.3	0.007	"		
AF-50	0.60		Av 135	Av 4.7	0.006	"		
AF-30	0.40		Av 120	Av 4.2	0.005	"		
Gelman GM-1	5.0	1.49				Dry 176		
GM-3	1.2	1.49				176		
GM-4	0.80	1.49				176		
GM-6	0.45	1.49				176		
GM-8	0.20	1.49				176		
GM-9	0.10	1.49				176		
GM-10	0.05	1.49				176		

*Alternate value reported

Table 4-52. Membrane filter media.

Another filter that should be discussed is the Nucleopore membrane filter. These filters have been reported to have high efficiencies, but even filters with 0.8 μg holes are not very efficient (10). The Nucleopore membranes also have the disadvantage of an extremely high pressure drop across the filter. The pressure drop is almost double that of the Millipore membrane filter. The codes used by filter manufacturers are shown in Figure 4-53.

Code	Manufacturer
IPC	Institute of Paper Chemistry (U.S.A.)
S&S	Schleicher and Schuell (Germany)
Whatman	W. and R. Balston Ltd. (England)
H&V	Hollingsworth and Vose (U.S.A.)
MSA	Mine Safety Appliances Co. (U.S.A.)
Gelman	Gelman Instrument Co. (U.S.A.)
Millipore	Millipore Filter Corp. (U.S.A.)
C.W.S.	Chemical Warfare Service (Chemical Corps, U.S.A.)
AEC	Atomic Energy Commission (U.S.A.)

Figure 4-53. Filter manufacturers code.

Analysis Considerations

Figure 4-54 lists the effects of various chemicals on membrane filters. This listing should be quite helpful in setting up an analysis procedure.

Solvent	Effect on filter
Hydrocarbons	
Pentane	None
Hexane	None
Petroleum ether	None
Benzene	None
Toluene	None
Xylene	None
Halogenated hydrocarbons	
Methylene chloride	None
Ethylene chloride	Shrinks
Carbon tetrachloride	None
Trichloroethylene	None
Freon TF	None
Dichloroethane	None
Alcohols	
Methanol	Dissolves
Ethanol	Swells
Propanol	Distorts
Isopropyl alcohol	None
Butyl alcohol	None
Glycerol	None
Ether alcohols	
Carbitol	Dissolves
Methyl cellusolve	Dissolves
Butyl cellosolve	Dissolves
Ketones	
Acetone	Dissolves
Methyl ethyl ketone	Dissolves
Methyl isobutyl ketone	Dissolves
Cycohexanone	Dissolves
Diacetone	Dissolves

Figure 4-54. Membrane filter solubility characteristics. (Continued next page.)

Solvent	Effect on filter
Esters	
Methyl acetate	Dissolves
Ethyl acetate	Dissolves
Propyl acetate	Dissolves
Butyl acetate	Dissolves
Miscellaneous organic	
Pyridine	Dissolves
Dimethyl formamide	Dissolves
Unsymmetrical dimethyl hydrazine	Dissolves
Nitro benzene	Dissolves
Ethylene glycol	None
Varsol[1]	None
Cobehn[2]	None
Mineral spirits	None
Turpentine	None
JP-4	None
JP-5	None
Kerosene	None
Acids	
Glacial acetic acid	Dissolves
10% acetic acid	None
6N Hydrochloric acid	None
6N Sulfuric acid	None
6N Nitric acid	None
Alkalis	
6N Sodium hydroxide	Disintegrates
6N Ammonium hydroxide	None

[1] Reg. T. M. of Esso Standard
[2] Reg. T. M. of Cobehn Corporation

Figure 4-54. Membrane filter solubility characteristics, continued.

	(g/m^3)							
Item	Total particulates		Sulfates		Nitrates		Organics	
Dates	pH 6.5	pH 11	pH 6.5	pH 11	pH 6.5	pH 11	pH 6.5	pH 11
7-26	68.9	79.3	6.0	11.1	0.8	3.4	8.9	5.9
7-27	49.8	58.3	4.5	7.9	1.3	2.0	5.2	3.4
7-28	61.4	78.9	4.4	8.3	0.4	1.3	3.8	3.1
7-29	66.7	104.1	5.0	12.2	1.9	4.9	6.2	6.1
7-30	104.5	113.7	6.8	9.1	1.9	3.5	6.9	4.9
7-31	83.1	94.4	6.7	10.1	1.6	3.6	5.7	5.2
8-2	44.5	50.9	4.6	6.5	0.7	2.2	3.3	3.3
8-3	43.3	49.6	4.6	7.2	0.3	1.1	3.7	2.7
8-4	79.8	94.5	5.8	10.9	1.0	3.6	5.5	4.4
Mean	66.89	80.41	5.38	9.26	1.10	2.84	5.47	4.33

Alkaline filters yielded significantly higher results for total particles, nitrates and sulfates, but not organics. The difference is ascribable to the adsorption of acid gases.

Figure 4-55. Effect of glass fiber pH on concentration observed with 24-hr. standard high volume sampling in Anderson, Calif., July-Aug., 1972.

Filter	Size, mm[h]	No. of trials	Flow rate cfm[a]	Overall pressure drop, cm. Hg	Efficiency by CNC, %[h]
None	90 (holder only)	1	4.3 (max)	25.0	
			3.0	10.3	
			2.5	8.0	
None	90 + 47 (holder only)	1	4.2 (max)	26.6	
			3.0	9.0	
			2.5	6.9	
Membrane filters					
0.8 μ Nucleopore	47	2	1.5 (max)	50.8	72 ± 1[c]
5 μ Nucleopore	47	1	3.0	11.5	< 50
3.0 μ MF millipore (SS)	47	1	3.4 (max)	32.2	
			3.0	25.6	[f]
			2.5	19.9	98
3.0 μ MF millipore (SS)	90	2	4.1 ± 2(max)	26.3 ± 2.1	
			3.0	14.2 ± 2.4	96 ± 2
			2.5	10.8 ± 1.8	98
5.0 μ MF millipore (SM)	47	1	3.7 (max)	31.7	
			3.0	22.6	96
			2.5	17.6	
5.0 μ MF millipore (SM)	90	1	4.4 (max)	23.2	
			3.0	11.4	98
			2.5	8.6	98
8.0 μ MF millipore (SC)	47	2	4.0 (max)	27.1	
			3.0	16.5	97 ± 1
			2.5	13.1	97 ± 1
Gelman GA-1.5 μ cell. acetate	47	2	3.8 ± 0.1 (max)	30.2 ± 0.7	
			3.0	20.2 ± 0.2	98
			2.5	15.6 ± 0.2	97 ± 2
1.2 μ Silver membrane[g]	47	2	3.6 ± 0.2	29.3 ± 0.5	
			3.0	20.8 ± 2.7	
			2.5	16.4 ± 1.4	66
S&S 0.45 μ (B6A) cellulose acetate	47	1	1.5 (max)	53.1	ND
			1.0	41	ND
Teflon fiber filters					
5.0 μ Teflon millipore (LS)	90	2	3.2 ± 0.1 (max)	36.6 ± 0.6	
			3.0	30	
			2.5	24.8 ± 1.6	
			2.0	16.0	93
5 μ Teflon millipore (LS)	47	1	1.7 (max)	55	
10 μ Teflon millipore (LC)	90	1	4.7 (max)	26	
			3.0	10.8	73
			2.5	8.6	

Figure 4-56. Initial filtration efficiency and flow behavior of the Lundgren impactor as a function of the after filter media[d,e], continued.

Filter	Size, mm[h]	No. of trials	Flow rate cfm[a]	Overall pressure drop, cm. Hg	Efficiency by CNC, %[b]
Glass fiber filters					
Gelman A	47	2	3.9 ± 0.3 (max)	27.9 ± 1.1	
			3.0	17.6 ± 2.5	95
			2.5	13.1 ± 1.5	98
Reeves Angel #900 AF	47	1	4.1 (max)	23.2	
			3.0	11.4	98
			2.5	8.6	98
MSA 1106 BH	47	1	4.2 (max)	26.4	
			3.0	14.8	99
			2.5	11.2	98
S&S #25 acid washed	47	2	3.6 ± 0.2 (max)	29.9 ± 0.7	
			3.0	21.6 + 2.6	59
			2.5	16.0 ± 2.0	50 ± 12
S&S green ribbon #599	47	1	3.2 (max)	32.9	
			3.0	28.1	
			2.5	20.5	60
TFA	47	2	3.7 ± 0.3 (max)	29.6 ± 1.0	
			3.0	20.1 ± 2.7	66
			2.5	14.8 ± 1.9	52 + 14
Whatman 41	47	1	3.7 (max)	31.0	
			3.0	21.2	70
			2.5	16.0	81

a. Determined with built in flowmeter of Lundgren Impactor.

b. **Efficiency of particle removal as measured by a GE portable condensation nuclei counter. The condensation nuclei counter (CNC) works on much the same principle as a cloud chamber. The particle laden gas is** entered into a chamber. Inside the chamber is a light source. The inside atmosphere is saturated with water vapor. When the gas is suddenly expanded, the particles act as condensation nuclei, having water droplets form around them. The droplets are counted by a light scattering technique.

c. Measured at 1.2 l/min with the filter holder attached directly to CNC

d. Face velocity at 3.0 cfm ≅89 cm/sec for 47 mm filter and ≅30 cm/sec for 90 mm filter.

e. The impactor stages were neither covered by film nor rotated.

f. Results erratic at this high Δp.

g. Selas Flotronics

h. The effective size for the filters was 45 mm and 78 mm for 47 and 90 mm filters, respectively.

Figure 4-56. Initial filtration efficiency and flow behavior of the Lundgren impactor as a function of the after filter media[d,e].

Membrane and Teflon fiber filters											
Filter			% Efficiency for removal of particles of equivalent spherical diameters, μ								
	Size, mm	No. of trials	0.32	0.4	0.5	0.64	0.8	1.0	1.3	1.6
0.8 μ Nucleopore	47	1	82	96	99	99	100	100	100	100
5.0 μ Nucleopore	90	1	83	95	98	97	98	100	100	100
3.0 μ MF millipore (SS)	90	3	99.93	99.98	100	100	100	100	100	100
5.0 μ MF millipore (SM)	47	1	100	100	100	100	100	100	100	100
5.0 μ MF millipore (SM)	90	1	100	100	100	100	100	100	100	100
5.0 μ Teflon millipore (LS)	90	1	99	99.6	100	100	100	100	100	100
8.0 μ MF millipore (SC)	47	1	96	99	99	99	96	99	100	
10 μ Teflon millipore (LC)	90	1	96	99	99	99	100	100	100	100
1.2 μ Silver membrane	47	2	99.9	100	100	100	100	100	100	100
S&S 0.45 (B6A) cellulose acetate	17	1	100	100	100	100	100	100	100	100
Gelman GA 1 cellulose acetate	47	1	99	100	100	100	100	100	100	100
Glass fiber filters										
Gelman A	47	2	99.8	99.8	99.6	99.7	99.1	99	99	97
Gelman A	25	1	100	100	100	100	100	100	100	100
Gelman A acid washed	25	1	99.9	100	100	100	100	100	100	100
Reeves angel # 900AF	47	1	99.9	100	99.9	100	100	100	100	100
MSA 1106BH	47	1	100	100	100	100	100	100	100	100
S&S #25 acid washed	47	3	26	53	65	64	69	71	79	88
TFA[b]	47	2	38	67	80	81	83	85	84	87
Whatman 41	47	1	63	83	90	84	89	81	94	100
S&S green ribbon #559	47	1	69	84	88	87	93	98	97	100

a. Face velocity, cm sec. for 25, 47 and 90 mm filters is 0.82, 0.31 and 0.11, respectively.

b. After sampling 500 ft³ of room air, the filtration efficiency of TFA increased to 90% for 0.3μ particles with other values in the range 80-90% for sizes up to 1.6μ. This efficiency was not significantly altered by discharging the filter over a radioactive source.

Figure 4-57. Initial efficiency of filtration of particle ≥ 0.3μ diameter via Royco particle counter[a].

	PS	DMS	W41	C	HAWP025	HAWP047	AAWP025	AAWP047	EHWP047	GA-6
Cl	3,000	27,000	100	300	1,000	1,000	1,700	1,000	1,000	600
Br	25	1,000	5	20	4	3	<5	<2	6	4
S	[a]	± 30,000		6,000			4,800			
Na	80	90	150	700	600	330	520	400	1,800	2,200
K	20	8	15	200	130	100	120	100		
Mg	<200	<1,500	<80	2,400	<300	<200	400	200		
Ca	300	300	140	3,800	670	250	500	370	570	1,250
Ba	7,000	<500	<100	<100	<100	<100	<100	<100		
Al	20	20	12	200	20	10	15	10	60	740
Sc	0.04	<0.01	<0.05	0.2	<0.05	<0.01	<0.91	<0.05		
Ce	<0.4	<1	<0.5	<0.3	<0.5	<1	<0.5	<0.3		
La	<0.2	<0.1	<0.2	<0.3	<0.1	<0.2	<0.5	<0.2		
Ti	10	70	10	50	15	5	10	<10		
Fe	100	85	40	300	40	<300	80	40		
Mn	1	2	0.5	80	7	2	2.5	2	6	2
Co	0.2	0.2	0.1	0.8	0.2	<1	0.4	0.1		
Ni	25	<25	<10	60	<8	<50	14	<20		
Ag	<2	<2	2	3	<4		<3	<1		
Cu	10	320	<4	90	20	40	85	60	25	30
Zn	60	515	<25	30	25	20	10	7		
Sb	2.5	1	0.15	0.5	0.5	3	0.4	1		
Cr	5	2	3	12	15	14	20	15		
Hg	3	1	0.5	3	<0.4	<1	<1	0.5		
V	0.06	<0.6	<0.03	0.5	<0.06	0.09	<0.2	<0.05	<0.05	<0.05

[a] Not determined.

Figure 4-58. Filter impurity levels (ng/cm²) for various filters.

One advantage of membrane filters is that they are primarily surface collectors, consequently, the problem of self-absorption of radiation becomes negligible, although the difference in the two sides of Millipore filters must be taken into consideration in alpha spectroscopy.

The membrane filters lend themselves very readily to particle size analysis by microscopy. By using an immersion oil with an index of refraction (N_D) equal to that of the filter (see Figure 4-52), the filter can be made transparent to light, thus allowing light-transmitted microscopic analysis. However, care must be taken to ensure that the N_D of the particle is not the same as the N_D of the immersion oil.

The filters can also be readily ashed and leave very little residue. This can be a definite advantage in some analysis schemes. Most membrane filters are also readily soluble in many organic solvents, thus allowing removal of particulate matter with little problem.

Sample Problems

Problem 1

A filter is to be chosen for subsequent analysis by a chemical ashing technique. The maximum vacuum flow resistance the pump can overcome is about 10 in. of water when the face velocity is about 100 ft. min. When dealing with atmospheric sampling, the temperature is not a limiting factor since most filters will operate at temperatures over 100°C (212°F). Which filter, based on the available information and assuming all were at hand, would be the best choice?

Solution

From Figures 4-50 and 4-51 it can be seen that glass fiber and mixed fiber filters have relatively high ash contents, making them impractical for chemical ashing. From Figures 4-49 and 4-52, it can be seen that cellulose fiber filters and membrane filters exceed the requirements of the pumps. From Figure 4-49, it can be seen that Whatman 41, S&S 604, MSA BM-2133, and the IPC 1478 all have ash contents less than 1% and flow resistances less than 10 in H_2O. These would all be acceptable and availability would determine which would be used.

Problem 2

The pump capacity from Problem 1 has now been doubled so that 20 in. H_2O@100 ft. min. can now be sampled. An efficiency of 100% for all particles down to 0.3 μ is desired. Which filter should be used?

Solution

From Figure 4-57, the 5.0 μ MF Millipore (SM) 47 mm & 90 mm, S&S B6A cellulose acetate, Gelman A 25 mm and MSA 1106 BH all show apparent particle efficiencies of 100% for all sizes. From Figure 4-50 both the Gelman and MSA filters show an ash content over 95%. The S&S B6A does not appear on Figures 4-49 through 4-52, but since the cellulose acetate is a mixed fiber filter we can assume the ash content is too high. From Figure 4-52, the 5.0 μ Millipore SM has a low ash content (0.0001%) and an acceptable flow resistance (19.8 in. H_2O).

Problem 3

A filter is needed for subsequent analysis by acid extraction. The sampling atmosphere is very humid. The flow resistance must be kept below 10 in. H_2O. Which filter should be used?

Solution

Cellulose filters are very hygroscopic so they should not be used in this situation. Membrane filters have extremely high flow resistances, so they, too, should not be used in this situation. Glass fiber filters are non-hydroscopic and are the filters of choice in water vapor laden atmospheres. By referring to Figure 4-50, Gelman G or M filters could be used since they both qualify for the low flow resistance requirements.

Summary

No single type of filter is the right one for all air sampling problems. In evaluating a filter one must consider many factors: general filter characteristics, collection efficiency, background filter impurities, sampling conditions, ease of analysis, self absorption, flow resistance, and the purpose for which the sample is being taken.

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Chapter 5

Gaseous Sampling

Principles of Absorption

Introduction

Absorption of pollutants in various media plays an important role in air pollution monitoring. It is particularly important in the wet-chemical methods of analysis. Before the advent of continuous monitoring instrumentation, techniques employing absorption were the most inexpensive and up-to-date methods available.

Absorption is the process "of transferring one or more gaseous components into a liquid or solid medium in which they dissolve." Absorption of gaseous pollutants in solution is frequently utilized in atmospheric sampling because of the numerous methods available to analyze the resulting solution. These methods include photometric, conductimetric, and titrimetric techniques. Details of sampling and analysis of specific gaseous pollutants by absorption are given elsewhere. This discussion concentrates on a description of the gas-liquid absorption process and factors affecting collection efficiency. Devices frequently utilized in gas-liquid absorption and several current applications are also discussed.

Types of Absorption

In gas-liquid absorption the collecting liquid (i.e., the absorbent) may change either chemically or physically, or both, during the absorption process. In gas-liquid absorption sampling, two types of absorption have been recognized: (a) physical absorption and (b) chemical absorption.

A typical chemical absorption process would involve drawing a volume of air through a solution that reacts with the gaseous contaminant to form a nongaseous compound. For example, an acid mist is drawn through a volume of sodium hydroxide. The acid reacts with the base to form a stable salt. Titration of the unreacted base with standard acid indicates the quantity of pollutant reacted.

Physical Absorption (2, 3)

Physical absorption involves the physical dissolving of the pollutant in a liquid. The process is usually reversible in that the pollutant exhibits a relatively appreciable vapor pressure. The solubility of the pollutant in a given absorbent is dependent on the partial pressure of the pollutant in the atmosphere and the temperature and purity of the absorbent. An ideal solvent would be relatively nonvolatile, inexpensive, noncorrosive, stable, nonviscous, nonflammable, and nontoxic. In many cases distilled water fulfills many of these characteristics and is used as the solvent for collecting some gases. The suitability of distilled water for several selected gases is presented in Figure 5-1.

Gas	Volume absorbed per volume of water*
Nitrogen	0.015
Oxygen	0.031
Nitric oxide	0.047
Carbon dioxide	0.878
Hydrogen sulfide	2.582
Sulfur dioxide	39.374

*Gas volumes reduced to 0°C and 760 mm Hg

Figure 5-1. Solubility of selected gases in distilled water at 20°C.

The physical absorption process involves collecting the pollutant by solution in the absorbent. The solution is then analyzed for pollutant concentration by a convenient analytical method. In general, low efficiency will be obtained for physical absorption unless the pollutant is very soluble and the ratio of dissolved gas to liquid volume is small. For this reason, physical absorption is rarely the only absorption process involved in collecting gaseous pollutants.

Chemical Absorption (2, 3)

In contrast to physical absorption, chemical absorption is a process that involves a liquid absorbent that reacts with the pollutant to yield a nonvolatile product. The solvent selected is one that reacts with the pollutant in an irreversible fashion; for example, the reactions of ammonia and carbon dioxide gases with acidic and basic solvents, respectively. These reactions produce carbonic acid (H_2CO_3) and ammonium hydroxide (NH_4OH). The solubilities of these acids and bases are much greater than gaseous CO_2 or NH_3. Primary factors affecting the choice of an absorbent in chemical absorption are the solubility of the pollutant, reactive properties of pollutant and absorbent, and the subsequent analytical method to be used. Care should be taken to avoid an absorbent that will interfere with subsequent chemical analysis.

A typical process involving chemical absorption is the reaction of SO_2 and aqueous H_2O_2 to produce sulfuric acid. The concentration of SO_2 is determined by titrating the H_2SO_4 formed with Ba $(ClO_4)_2$. This procedure is currently the reference method for determining SO_2 emissions from stationary sources.

Collection Efficiency (2, 4)

Each absorption sampling device must be assembled from units found to be most suitable for the specific pollutant involved. It is not necessary to have 100 percent collection efficiency; however, the efficiency under sampling conditions should be known and reproducible. In some circumstances a sampling system having a relatively low collection efficiency (e.g., 60-70 percent) could be used provided that the desired sensitivity, reproducibility, and accuracy are obtainable.

There is much information available in the literature concerning optimum flow rates for specific pollutants and collection efficiencies with respect to the pollutant and absorbent for many sampling devices. However, much more information is needed on the variation of collection efficiency with the rate of sampling, concentrations of a variety of compounds, and the nature of the collecting medium. For available information on gas-liquid absorption theory and the mathematical treatment of the variables affecting collection efficiency, the reader is referred to the literature (Refs. 1-10). In the present discussion only a qualitative description of the factors affecting collection efficiency has been attempted.

Factors Affecting Collection Efficiency (2, 3, 4)

The variables affecting the collection efficiency of methods that use absorbers for the collection of gaseous contaminants may be conveniently considered as: (a) those associated with the absorber such as an acceptable flow rate, bubble size, and height of the liquid column: (b) the chemical characteristics of the sampling situation such as the chemical nature and concentration of the pollutant in the air and the absorbing medium, the chemical nature and concentration of the absorbing solution, and the reaction rate; and (c) the physical characteristics of the sampling situation such as temperature, pressure, and pollutant solubility.

Absorber Characteristics

The gas flow rate through the absorber is one of the major factors determining the collection efficiency of an absorber. Absorption collection efficiency varies inversely with the flow rate. An increase in the flow rate through the solution will decrease the probability of adequate gas-liquid contact. In addition, high flow rates increase the possibility of liquid entrainment in the effluent gas. If varying flow rates are used in sampling, a collection efficiency versus flow rate curve should be determined for each absorber and absorber type. All other variables (e.g., temperature, pollutant and absorbent types, etc.) should be held at the desired values.

The collection efficiency of the absorption process for a gas or vapor by chemical absorption or physical absorption depends on the probability of successful collisions of reagent or solvent molecules with gas molecules. For a given concentration of reagent this probability of collisions will depend on the surface area of the gas bubbles, on the length of the column of liquid through which the bubbles must pass, and on the rate at which they rise through the liquid. As the volume of individual bubbles decreases, the surface area presented to the liquid increases. Hence smaller bubbles have a greater possibility of gas transfer into the absorbent phase. For this reason many absorption devices use fritted discs as opposed to injection-type dispersion tubes to achieve a smaller bubble size. However, due to possible surface reactions that can take place at the frit, fritted bubblers may not be appropriate for certain types of sampling (e.g., for ozone). The length of the column of liquid in the absorber is another prime factor affecting the collection efficiency. The longer the gas bubble is in contact with the liquid, the more pollutant transferred. However, in many cases this variable cannot be used to its maximum advantage; for example, when the sampled pollutant has a low concentration in the atmosphere it must be collected in a small absorbent volume so that it is in the sensitivity range of the subsequent analytical method to be used. Bubble rise time is a function of bubble size and absorbent height. A compromise is usually reached by having the smallest feasible bubble size combined with the highest absorbent column possible for the particular analysis.

Chemical Characteristics

The best situation, with respect to collection efficiency, is to choose an absorbent with a very large capacity for absorbing the pollutant without building up appreciable vapor pressure. This can be accomplished by choosing a chemical reagent that reacts with the pollutant in an irreversible fashion. For example, the irreversible reaction that occurs when carbon dioxide is absorbed in a sodium hydroxide solution to form the carbonate ($CO_3^=$) ion.

The concentration of the absorbing medium to be used is a function of the expected concentration of the contaminant encountered, and the rate of the particular chemical reaction being used. An excess of the reactant in the absorbing solution is preferable to ensure that all the pollutant is collected and that the reaction rate is at a maximum. Ideally the reaction should be instantaneous since the period of contact between the pollutant and the absorbent is a short one.

Since the rate of reaction is proportional to concentrations of the reacting substances, other variables being equal, the rate of the process falls off as the reaction proceeds. This phenomenon must be compensated for by increasing the concentration of the absorbing liquid, thereby, forcing the reaction to approach completion rapidly.

Physical Characteristics

The primary physical characteristics affecting collection efficiency are pressure, temperature, and pollutant solubility in the absorbing medium. In many sampling situations, these variables are fixed by ambient conditions.

The solubility of the pollutant in the absorbing medium is related to its partial pressure (by Henry's law), and the partial pressure of the pollutant in turn is related to its concentration. The net effect considering ideal gas behavior is that an increase in pollutant concentration in the air will result in an increase in pollutant solubility in the liquid. Increased pollutant solubility, other variables being equal, results in a higher collection efficiency.

An increase in temperature enhances chemical reactions but decreases pollutant solubility in the absorbent. In most cases the net effect is a decrease in collection efficiency with increasing temperature.

Determination of Collection Efficiency (2, 4)

The method of determining collection efficiency will depend on how the results are to be used. If the most accurate values are needed, the best available method for determining collection efficiency should be used. On the other hand, if only approximate values are needed, a less stringent method for determining collection efficiency may be satisfactory. In all cases collection efficiency should be defined with respect to the method of determination.

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The most accurate method of determining the collection efficiency of a particular absorber is by a trial on a synthetic atmosphere duplicating in every respect the actual sampling conditions. Calibration techniques consist of both dynamic dilution and static dilution systems. In dynamic dilution a continuous supply of a known pollutant concentration is available that can be sampled, while the static system consists of a container holding a known volume of pollutant of a known concentration. In both of these calibration procedures the investigator must be assured that the atmosphere being sampled actually contains the pollutant concentration it is believed to contain.

Another method that may be used for collection efficiency calibration is the comparison of the technique of interest to a previously calibrated method. In this technique the conditions of the calibrated method are imposed on the method of interest. All variables in both methods should be identical, especially with respect to interferences.

Absorption Devices (2, 11)

A variety of devices have been used for sampling pollutants from the atmosphere. One of the simplest and most common devices used is an ordinary gas washing bottle containing the absorbent plus a gas dispersion tube for introduction of the pollutant into the solution. A typical device of this type is illustrated in Figure 5-2.

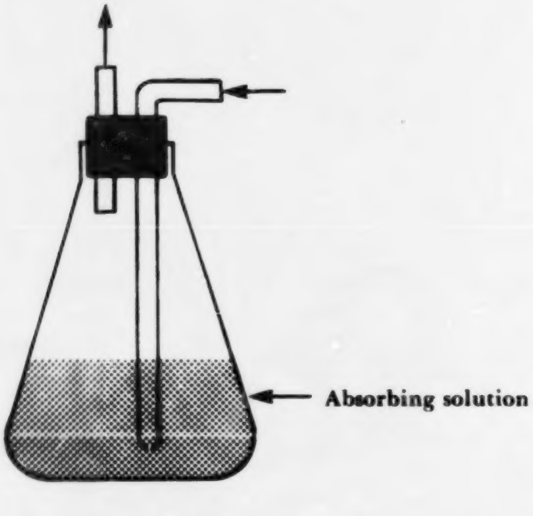

Figure 5-2. Absorption device adapted from an Erlenmeyer flask.

Gas flows from the unrestricted opening into the absorbent solution. A variety of absorbers of this type are available. They are usually glass and may be conical or cylindrical in shape. Typical flow rates through the various devices range from 1 to 5 liters per minute.

The majority of other absorption devices used in atmospheric sampling fall into two categories: (a) fritted-glass absorbers and (b) impingers.

Fritted-Glass Absorbers

A great variety of shapes and sizes of these absorbers are being used. A few are illustrated in Figure 5-3.

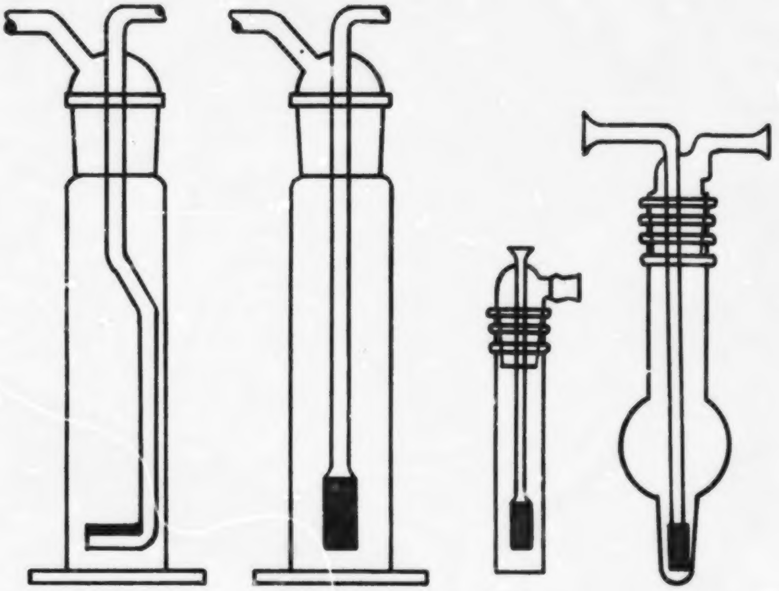

Figure 5-3. Typical fritted-glass absorbers.

These units usually provide the most efficient collection of gaseous pollutants. In addition to the commercially available units, homemade devices may be created using normal gas dispersion tubes. The fritted part of the dispersion tube is readily available in the form of a disc or cylinder of various pore size. The coarse and extra coarse frits provide good pollutant dispersion with a minimum head loss.

The collection efficiency of any one device will depend on the factors previously mentioned. However, under optimal conditions of flow rate, absorbing medium and pollutant type, many of the fritted-glass absorbers have a collection efficiency in excess of 90 percent. Several of their more important characteristics are presented in Figure 5-4.

Principle of operation	Devices	Capacity (ml)	Sampling rate ℓ/min	Efficiency* %	Comment	Cost	Source
Simple gas-washing bottles. Gas flows from unrestricted opening into solution. Glass, conical or cylindrical shape	Standard	125 – 500	1 – 5	90 – 100	Bubblers are large. Reduction of sampling rate increases efficiency. Several units in series raises efficiency	$ 6.00 9.00	Pyrex
	Drechsel	125 – 500	1 – 5	90 – 100	Similar to above	4.00 6.00	Fisher
	Fleming	100	1 – 5	90 – 100	Difficult to clean	3.65	A. H. Thomas
Modified gas-washing bottles	Fritted bubbler	100 – 500	1 – 5	95 – 100	Fritted tubes available for simple gas washing, items above. Smaller bubblers provide increased gas-liquid contact		A. H. Thomas
	Glass bead bubbler	100 – 500	1 – 5	90 – 100	Provides for longer gas-liquid contact smaller bubbles		Self constructed
Large bubbler traverses path extended by spiral glass insert.	Fisher Milligan bottle	275	1 – 5	90 – 100		7.25	Fisher
	Greiner-Friedrichs	100 – 200	1 – 5	90 – 100	Similar to Fisher Milligan	12.00 13.00	Sci Glass
Impingers – designed principally for collection of aerosols. Used for collection of aerosols	Greenburg Smith	500	1 – 5	90 – 100	Cylindrical shape	28.00	Sci. Glass
Used for collection of gases. Restricted opening. Fritted tubes available which allow use as bubbler	Midget	100	.1 – .5	90 – 100		7.50	Sci. Glass
Smog bubbler	Fritted bubbler	10 – 20	1 – 4	95 – 100		18.00	Ace Glass

*Under optimum conditions of flow rate, absorbing medium etc. for a particular pollutant.

Figure 5-4. (11) Absorption sampling devices.

Absorbers that use frits with a pore size of approximately 50 micrometers or less gradually become clogged with use. They may be cleaned by surging the appropriate cleaning solution back and forth through the frit and then rinsing with distilled water in the same fashion. Various substances may be removed from the frits by cleaning with the appropriate solvent (e.g., hot hydrochloric acid for dirt, hot concentrated sulfuric acid containing sodium nitrite for organic matter, etc).

Impingers

Impingers are often used in sampling for gaseous and vaporous pollutants from the atmosphere. Two types of impingers are shown in Figure 5-5.

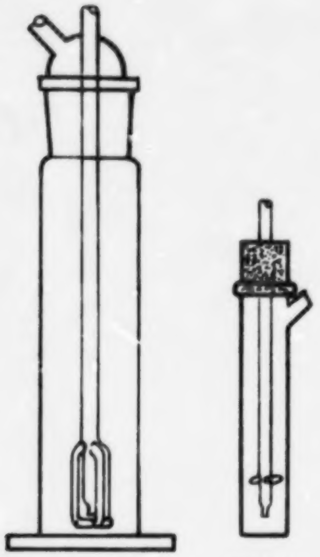

Figure 5-5. Two types of impingers.

A limited amount of investigation has indicated that the impinger is somewhat less efficient than the fritted absorber for collecting gaseous pollutants. When several types of absorbers were operated under optimal conditions, the midget impingers were found to be less efficient than the fritted-glass absorber. In addition, the threshold concentration for collection with the midget impinger was found to be somewhat higher than that for several types of fritted-glass absorbers.

Summary

Gas-liquid absorption is the process by which a gaseous pollutant is dissolved in a liquid medium. If a chemical reaction occurs between the pollutant (absorbate) and absorbent, the process is termed chemical absorption, whereas, physical solution of the pollutant in the absorbent is termed physical absorption.

The collection efficiency of any particular absorption process is a function of the characteristics of the absorption device, and the chemical and physical properties of the absorbate-absorbent pair. A collection efficiency should be determined for each sampling analysis situation by a method that gives the accuracy desired.

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Principles of Adsorption

Basic Principles

Adsorption is the phenomenon by which gases, liquids, and solutes within liquids are attracted, concentrated, and retained at a boundary surface. The boundary surface may be the interface between a gas and liquid, liquid and liquid, gas and solid, liquid and solid, or solid and solid. Of the various boundary surfaces, the adsorption mechanism between liquid and solid, and gas and solid have received the most attention. The former with respect to removal of substances from solution with a solid adsorbent (e.g., purification), and the latter with respect to removing gaseous pollutants on solid adsorbents of high surface area (1).

A solid adsorbent has a crystal lattice structure. The atoms at the surface of the lattice are arranged in a regular sequence, which depends on the particular solid's crystalline structure. The valence or other attractive forces at the surface of a solid are unsatisfied or unsaturated because they are not united with other atoms. As a result of this unbalanced condition, the solid surfaces will tend to satisfy their residual forces by attracting and retaining gases or other substances with which they come in contact. This surface concentration of substance is the adsorption process. The attracted substance is known as the adsorbate, while the surface substance is called the adsorbent.

In air pollution work, adsorption techniques are commonly used for collecting a specific gas or combination of gases. A typical process consists of passing a gas stream through a container filled with an adsorbent such as activated charcoal, alumina, or silica gel. The gas is bound to the adsorbent by molecular forces and, if condensation does not occur, the gas remains physically and chemically unchanged. Following collection, the gas may be removed from the absorbent for analysis or ultimate deposition by applying heat, passing inert carrier gases through the system, or treating chemically.

Adsorption can be distinguished from absorption. In absorption the material is not only retained on the surface, but it passes through the surface and is distributed throughout the absorbing medium. The term absorption in many cases implies a chemical reaction between the absorbing medium (absorbent) and the collected substance (absorbate). For example, water is absorbed by a sponge and by anhydrous calcium chloride. However, various gases are [illegible] surface of activated carbon. Often when the true process is not known the term sorption is used. (2, 3)

Types of Adsorption

Investigation of the adsorption of gases on various solid surfaces has revealed that the operating forces are not the same in all cases. Two types of adsorption have been recognized: (a) physical or van der Waals' adsorption (physiosorption) and (b) chemical adsorption (chemisorption).

Physical Adsorption

In physical adsorption, the attractive forces consist of van der Waals' interactions, dipole-dipole interactions, and/or electrostatic interactions. These forces are similar to those causing the condensation of a gas to a liquid. The process is further characterized by low heats of adsorption, on the order of 2-15 kilocalories per mole of adsorbate, and by the fact that adsorption equilibrium is reversible and rapidly established.

Physical adsorption is a commonly occurring process. For example, this is the type of adsorption that occurs when various gases are adsorbed on charcoal. If the temperature is low enough, any gas will be physically adsorbed to a limited extent. The quantity of various gases adsorbed under the same conditions is roughly a function of the ease of condensation of the gases. The higher the boiling point or critical temperature* of the gas, the greater is the amount adsorbed. This concept will be discussed in more detail subsequently.

Chemical Adsorption

In contrast to physical adsorption, chemical adsorption is characterized by high heats of adsorption, on the order of 20-100 kilocalories per mole of absorbate, which leads to a much stronger binding of the gas molecules to the surface. Heats of adsorption are on the same order of magnitudes as chemical reactions and it is evident that the process involves a combination of gas molecules with the adsorbent to form a surface compound. This type of adsorption resembles chemical bonding and is called chemical adsorption, activated adsorption, or chemisorption. For example, in the adsorption of oxygen on tungsten it has been observed that tungsten trioxide distills from the tungsten surface at about 1200°K. However, even at temperatures above 1200°K, oxygen remains on the surface, apparently as tungsten oxide. Additional examples of chemical adsorption are the adsorption of carbon dioxide on tungsten, oxygen on silver, gold on platinum, and carbon and hydrogen on nickel.

A comparison of physical and chemical adsorption can be made by considering the adsorption of oxygen on charcoal. If oxygen is allowed to reach equilibrium with the charcoal at 0°C, most of the oxygen may later be removed from the charcoal by evacuating the system at 0°C with a vacuum pump. However, a small portion of the oxygen cannot be removed from the charcoal no matter how much the pressure is decreased. If the temperature is now increased, oxygen plus carbon monoxide and carbon dioxide are released from the charcoal. Thus most of the oxygen is physically adsorbed and can be easily removed, but a small quantity undergoes a chemical reaction with the adsorbent and is not readily removed. In some cases, chemical adsorption may be preceded by physical adsorption, the chemical adsorption occurring after the adsorbent has received the necessary activation energy.

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*Critical temperature may be defined as that temperature above which it is impossible to liquify a gas no matter how high an external pressure is applied.

In general, with respect to the adsorbent-adsorbate pairs, chemical adsorption is more specific in nature than physical adsorption. It is usually a much slower process, requiring the displacement or selection of the molecules where the reaction is to occur. The chemisorption process is enhanced at higher temperatures where existing energy barriers between the adsorbent and adsorbate are overcome. At low temperatures, chemical adsorption in some systems may be too slow to reach a measurable amount. In many cases the adsorption occurring is a combination of both types. At low temperatures physical adsorption may predominate, whereas at higher temperatures chemisorption may be more prominent. This situation is true for the adsorption of hydrogen on nickel. However, because of the non-specificity of van der Waals' forces, physical adsorption may be occurring but be hidden by chemisorption. Finally, chemical adsorption is usually limited to the formation of a single layer of molecules on the adsorbent's surface (monolayer adsorption), whereas in physical adsorption the adsorbed layer may be several molecules thick (multilayer adsorption).

In most of the adsorption equipment in air pollution control work, physical adsorption plays the most prominent part (2, 3, 4).

Variables Affecting Gas Adsorption

The quantity of a particular gas that can be adsorbed by a given amount of adsorbent will depend on the following factors: (a) concentration of the gas in the immediate vicinity of the adsorbent; (b) the total surface area of the adsorbent; (c) the temperature of the system; (d) the presence of other molecules competing for a site on the adsorbent; (e) the characteristics of the adsorbate such as weight, electrical polarity, chemical reactivity. Ideal physical adsorption of a gas would be favored by a high concentration of material to be adsorbed, a large adsorbing surface, freedom from competing molecules, low temperature, and by aggregation of the adsorbate into a form that conforms with the pore size of the attracting adsorbent (5, 6).

Several of the above listed variables will not be discussed in greater detail.

Adsorption Isotherms

Adsorption processes where physical adsorption rather than chemisorption represents the final state can be explained in terms of equilibrium measurements. For a given amount of adsorbent with a given surface area the amount of gas adsorbed is dependent on the pressure (or concentration) of the gas surrounding the adsorbent. The higher the pressure or concentration of the gas at a given temperature, the greater the amount of gas adsorbed. When an adsorbent and gas are mixed, the amount adsorbed will gradually increase while the concentration of the adsorbate in the system decreases until the rate of adsorption becomes equal to the rate of desorption. Thus an equilibrium between the two reactions is established. If additional gas is added to the system the amount adsorbed will increase until equilibrium is again established. Likewise, if the gas concentration is decreased the adsorbent will lose gas to its surroundings until equilibrium is again reached.

The description of the relationship between the quantity of gas adsorbed at various concentrations or pressures at constant temperature is called an adsorption isotherm. An adsorption isotherm consists of a plot of the data obtained from measuring the amount of gas adsorbed (e.g., grams adsorbed per gram of adsorbent) at various gas concentration or pressure (e.g., moles per liter or atmospheres), as the case may require, at equilibrium under a condition of constant temperature. Adsorption isotherms are useful in that they provide a means of evaluating: (a) the quantity of gas adsorbed at various gas concentrations; (b) adsorptive capacities at various gas concentrations; (c) the adsorptive capacity as a function of concentration and type of gas; and (d) the surface area of a given amount of adsorbent (1, 2, 3).

Types of Adsorption Isotherms (1, 3)

The graphic plots of adsorption isotherms yield a wide variety of shapes. Six general types of isotherms have been observed in the adsorption of gases on solids; these are illustrated in Figure 5-6. In physical adsorption all six isotherms are encountered, while in chemisorption only type 1 occurs.

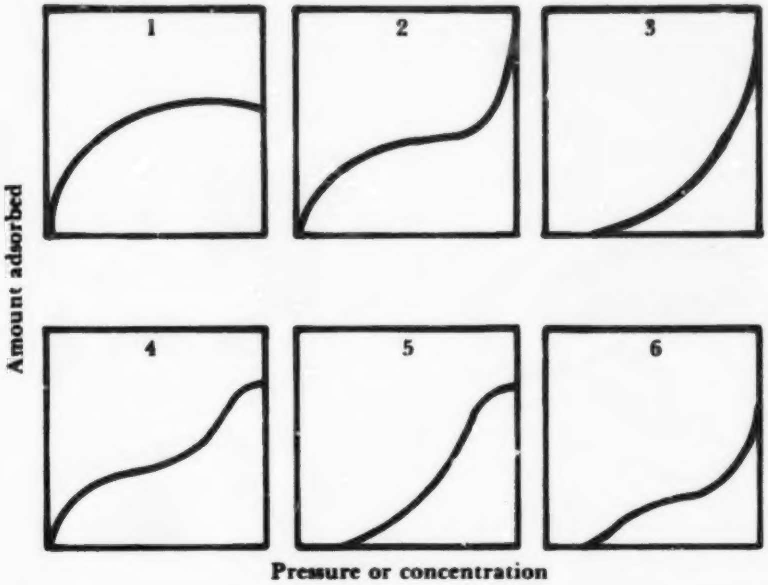

Figure 5-6. Gas adsorption isotherms.

Type 1—This type represents the adsorption of a single layer of gas molecules on the adsorbent. There is no interaction between the adsorbed molecules.

Type 2—This isotherm begins like type 1 but is modified at high pressure by multilayer adsorption. There is definite interaction between the layers of adsorbed gas molecules.

Type 3 – This type of isotherm is rare. It occurs only when initial adsorption favors a very few strong sites. The interaction between adsorbed molecules is so strong that vacant sites next to occupied sites are stronger than any other vacant sites. In this type of adsorption the number of effective sites increases with coverage of the adsorbent.

Type 4 & 5 – These two are similar to types 2 and 3 respectively, except that they continue to exhibit adsorption at high adsorbent coverage.

Type 6 – This type resembles type 3 with monolayer adsorption first and then continued deposition of a multilayer film.

Adsorbate Characteristics

The major adsorbate characteristics affecting the amount of gas adsorbed are the ease of liquefaction of the gas, adsorbate size, concentration of the gas, and presence of other gases.

Gas Liquefaction

The specificity by which certain gases are adsorbed on solid adsorbents is illustrated in Figure 5-7, where the volumes of different gases adsorbed by one gram of charcoal at 15 °C are tabulated.

Gas	Volume adsorbed (cc)	Critical temperature (°K)
H_2	4.7	33
N_2	8.0	126
CO	9.3	134
CH_4	16.2	190
CO_2	48.0	304
HCl	72.0	324
H_2S	99.0	373
NH_3	181.0	406
Cl_2	235.0	417
SO_2	380.0	430

*Volumes of gases have been reduced to standard conditions (0 °C and 1 atmosphere pressure).

Figure 5-7 (3). Adsorption of gases on one gram of charcoal at 15 °C*.

Figure 5-7 indicates that the extent of adsorption parallels the increase in critical temperature. This correlation suggests that gases which liquify easily (high critical temperatures) are more readily adsorbed. However, it does not imply that the adsorbates exist as liquids on the adsorbent's surface. A similar relationship is obtained with boiling points (3).

Adsorbate Size

The size of the gas molecule to be removed by adsorption is characterized by a lower and upper range. The lower size limit is imposed on physical adsorption by the requirement that the pollutant must be higher in molecular weight than the normal components of air. In general, gases with molecular weights greater than 45 are readily removed by physical adsorption. This size includes most odorous and toxic gases of air pollution interest. Gases of interest of lower molecular weight, such as formaldehyde and ammonia, may be removed by chemical adsorption methods using appropriately impregnated adsorbents.

For the upper limit the individual particles must be sufficiently small so that Brownian motion or kinetic velocities will ensure effective contact by collision between them and the granular adsorbent. Although moderate efficiencies may be obtained for very fine mists, the upper limit is generally in the range of molecular size.

Gas Concentration

As seen from the examination of adsorption isotherms, the quantity of gas adsorbed is a function of the gas concentration or pressure. An increase in concentration or pressure in the vicinity of the adsorbent results in an increase of the total amount of gas adsorbed.

Presence of Other Gases

Since the presence of additional gas molecules in a particular adsorbent-adsorbate system causes competition for the limited number of adsorption sites present, the observed effect is a reduction in the amount of adsorbate removed.

Adsorbent Characteristics

Most of the common adsorbents in use are more or less granular in form and are supported in a column through which the gas to be sampled is drawn. Common adsorbents have the capacity to adsorb 8–40 percent of their weight. An ideal adsorbent should be granular and of such size and form that it offers little or no resistance against flow. It should have a high adsorptive capacity; be inert and specific; be resistant to breakage, deterioration, and corrosion; be easily activated; and provide an easy release of adsorbate. Unfortunately, no one adsorbent possesses all these characteristics, so it becomes a matter of choosing the best adsorbent for a particular job (5, 7, 8,).

Surface Area

All solids are capable of adsorbing gases to some extent. However, since adsorption is a surface phenomenon, it is not very pronounced unless the adsorbent possesses a large surface area for a given mass. For this reason, materials like silica gel and charcoals obtained from wood, bone, coconut shells, and lignite are very effective adsorbing agents. Since large surface areas are desirable for extensive adsorption, this factor is of primary importance in determining the amount of absorbate that can be held by a unit of adsorbent. Solid adsorbents may vary in surface area from less than 1 to over 2,000 square meters per gram. Typical approximate surface areas of several adsorbents are presented in Figure 5-8. The latter two substances owe their high surface area to their porosity. They are thus capable of taking up large volumes of various gases.

Adsorbent	Area (m^2/g)
Clay	5 – 15
Asbestos	10 – 20
Chalk	20 – 30
Carbon black	50 – 100
Silica or alumina gel	200 – 800
Activated carbon	500 – 2000

Figure 5-8. Typical surface areas of adsorbents.

The extent of adsorption can be further increased by activating the adsorbents by various methods. For example, wood charcoal is activated by heating to between 350 – 1000 °C in a vacuum, in air, in steam, and/or in the presence of other gases to a point where the adsorption of carbon tetrachloride at 24 °C can be increased from 0.011 gram per gram of charcoal to 1.48 gram. The activation process involves distilling out various impurities from the adsorbent, thus leading to the formation of a larger free surface area for adsorption. Occasionally, large surface areas are produced by the original cellular structure of the plant, as in the case of coconut shell charcoal. However, the activation process will increase the porosity of the material and may, under some circumstances, cause it to be less stable as an adsorbent. For example, if the temperature is raised, the porous structure of the adsorbent may aggregate into larger units that tend to become smooth and inactive. In many cases the past history of the adsorbent with respect to preparation and method of activation is just as important as the chemical characteristics in determining the adsorption capacity (1, 3, 4).

Often the adsorbent will exhibit an inherent preference for the adsorption of certain gases. This preference is primarily due to such factors as the method of preparation and activation, and the chemical nature of the adsorbent's surface. Preparation and activation methods not only may increase total adsorptive capacity, but they may also affect the adsorption process with respect to adsorbate size.

Pore Size

The pore size in the more porous adsorbents may vary in diameter from a few to several hundred angstrom units. This may become a critical factor in selecting an adsorbent to remove a particular adsorbate. For example, iodine may be adsorbed on an adsorbent with a pore size of 10 Å in diameter, while methylene blue is excluded by pores having a diameter less than about 15 Å (1).

Chemical Nature

The chemical nature of the adsorbent's surface is an additional factor of considerable importance. It is of particular interest in chemical adsorption where a rapid rate and a large degree of chemical reaction is desirable. In physical adsorption the nature of the surface is one of the primary factors influencing the strength of the adsorbent-absorbate attraction. For example, a pure graphite surface physically adsorbs hydrophobic (i.e., water-hating) compounds to a large extent, while oxygenated surfaces are generally required to adsorb hydrophyllic (i.e., water-loving) compounds appreciably at room temperature (1).

Typical Adsorbents

The various adsorbents used in physical adsorption may be classified according to their degree of polarity. For example, activated carbon, which is commonly known as a non-polar adsorbent, is largely composed of neutral atoms of a single species exhibiting little polarity. The non-polar adsorbents are most effective for gross decontamination of moist air streams containing materials of little polarity (e.g., organic molecules).

The majority of the commercially important adsorbents other than carbon derivatives are simple or complex oxides. Their surfaces consist of heterogeneous distributions of charge on a molecular scale. They are strongly polar in nature. These adsorbents show a greater selectivity than do the carbon derivatives and exhibit a much stronger preference for polar than for non-polar molecules. In separation of various gases, the polar solvents are more useful than carbon derivatives. However, they are much less useful for overall decontamination of moist air streams, since the strongly polar water molecules are preferentially adsorbed (6).

Carbon

Various forms of carbon serve as efficient adsorbents. It has been shown that the material from which the carbon is prepared has a demonstrable effect upon the ability of the carbon to adsorb various gases. Carbon prepared from logwood, for instance, has approximately twice the capacity for adsorption as carbon from rosewood. Similarly, coconut shell is about twice as efficient as logwood. Strangely enough the carbon prepared from harder, denser materials such as peach and other fruit pits, and coconut shells have the highest adsorptive capacities. Primary carbon is not nearly as efficient as activated carbon. The adsorbents "activated charcoal," "active carbon," "adsorbent carbon," and "adsorbent charcoal" may be activated in a slightly different manner, but the terms are generally considered synonymous.

Activated carbon has a high adsorptive capacity, a high degree of hardness, high reliability and other premium qualities. Almost all volatile materials, whether they are chemicals or mixtures of odor-causing substances, are retained within the microscopic porous structure to some extent. The only gaseous materials that it will not adsorb very well are low molecular weight gases such as oxygen, nitrogen, and carbon monoxide. Activated carbon finds its major application in solvent recovery and odor removal. It is also employed to a limited extent in the removal and monitoring of hydrogen sulfide, sulfur dioxide, and other toxic gases. Activated carbon is perhaps the most widely used adsorbent in air pollution control. The following substances are some of those that have been shown to be appreciably adsorbed upon activated carbon:

acetic acid
benzene
ethyl alcohol
carbon tetrachloride
methyl alcohol
chloroform
acetone
acetaldehyde
mercury vapor
iodine
carbon disulfide
diethyl ether
ammonia
hydrochloric acid
nitrous oxide
carbon dioxide
noble gases
PVC

Molecular Sieve

Molecular sieve adsorbents* are synthetic sodium or calcium alumino-silicate zeolites of very high porosity. They are another representative of the siliceous adsorbents.

The structural formula of a typical molecular sieve is

$$\mathrm{Me}_{x/} \text{ [illegible] } \mathrm{O}_2)_y \bullet m\mathrm{H}_2\mathrm{O}$$

where Me represents exchange cations of charge n. The zeolite is precipitated as a white powder, bonded with clay, and formed into roughly spherical beads of four to twelve mesh size. The adsorbent is activated with heat to drive off water of hydration. The resulting product is a crystalline solid of very porous structure. Again the adsorptive characteristics are dependent on the method of preparation.

Molecular sieves can be made very specific with respect to pore size. This characteristic gives them the outstanding property of being specific on the basis of adsorbate size and shape. Molecular sieves show a strong preference for the more polar molecules. For example, these adsorbents will not adsorb organic molecules that match their pore size from a moist stream of air. The accompanying water molecules being adsorbed in preference. Molecular sieves are truly selective adsorbents because they can separate mixtures on the basis of differences in molecular size, degree of polarity, and extent of carbon bond saturation. In addition to their selective properties, molecular sieves possess a high adsorptive capacity over wide ranges of concentration and temperature. They also are capable of removing impurities to extremely low concentrations. These adsorbents have been tested successfully on carbon dioxide, hydrogen sulfide, acetylene, ammonia, and sulfur dioxide. They show promise for adsorption of compounds of low molecular weight (9).

Adsorption Losses in Air Sampling

Each adsorption medium used in atmospheric sampling has different limitations and problems. The problems most frequently encountered are:

- irreversible adsorption
- variable desorption efficiency
- interference by water vapor

Activated carbon is used extensively because of its high affinity for organic substances. Irreversible adsorption and variable desorption efficiencies are two principal problem areas associated with carbon sampling devices. Carbon can also serve as a potent catalyst creating the possibility of *in-situ* reactions during sampling.

Other alternative adsorption media that have recently been used extensively in air sampling are thermally stable, polystyrene divinyl benzene co-polymers (15, 16, 17). These media were used at ambient temperatures to collect volatile organic compounds. The volatile organics were recovered by thermal desorption followed by gas chromatographic analysis. These polymers are non-polar and have little affinity for water. Water desorption represents a severe problem in the analysis procedure. Adsorption sampling devices are being used primarily for the collection of volatile organic compounds.

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*Often referred to as molecular sieve absorbents.

Current Applications of Adsorption in Atmospheric Sampling

Carbon, porous polymers such as Porapack Q, Porapack P, Tenax GC, XAD-resins, and polyurethane foam have been used extensively in collecting pesticides, polychlorinated biphenyls, and other organic compounds in ambient air (18, 19, 20). These media can be used in sampling devices, which can be modifications of the hi-volume sampler (see Figure 5-9). Here polyurethane foam is used to collect organics, namely PCB's.

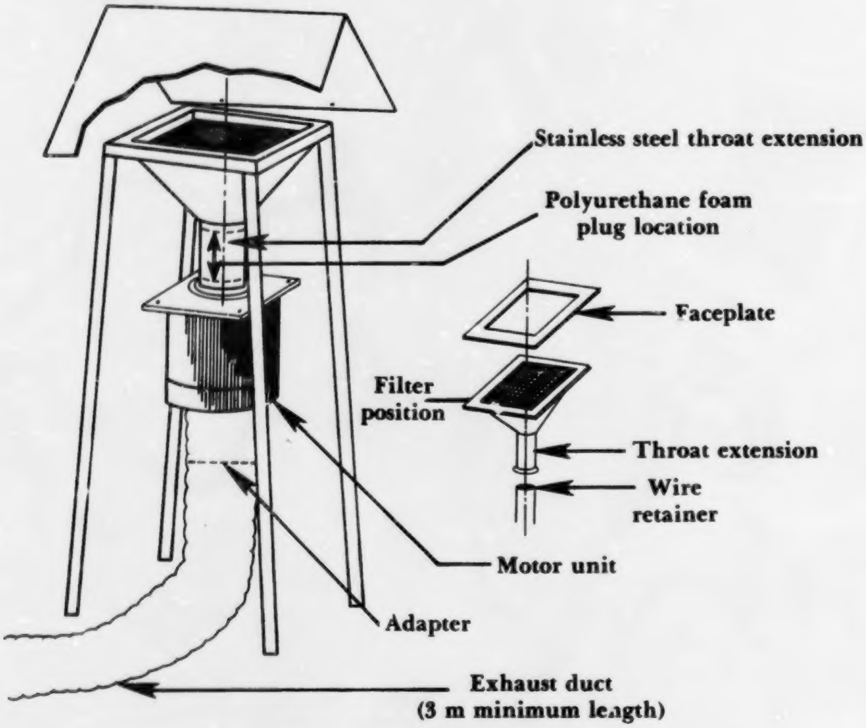
Stainless steel throat extension
Polyurethane foam plug location
Faceplate
Filter position
Throat extension
Wire retainer
Motor unit
Adapter
Exhaust duct (3 m minimum length)

Figure 5-9. Assembled sampler and shelter with exploded view of the filter holder.

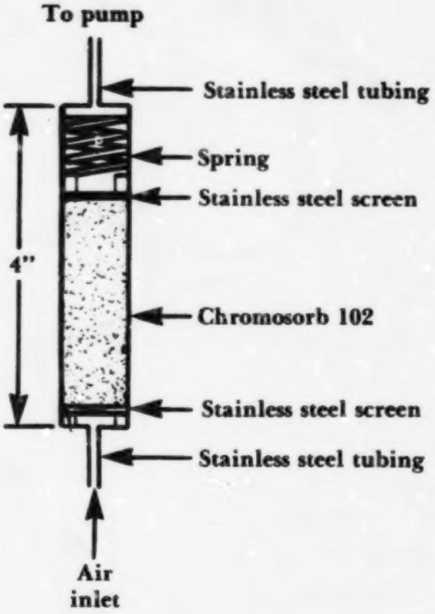
To pump
Stainless steel tubing
Spring
Stainless steel screen
4"
Chromosorb 102
Stainless steel screen
Stainless steel tubing
Air
inlet

Figure 5-10. High speed organic vapor collector.

Figure 5-10 illustrates an adsorbent sampling cartridge and Figure 5-11 shows a cartridge placed in a thermal desorption system. Figure 5-12 shows dynamic enrichment, which is repeated absorption from many different cartridges onto a single cartridge to attain enough of the specie of interest for measurement.

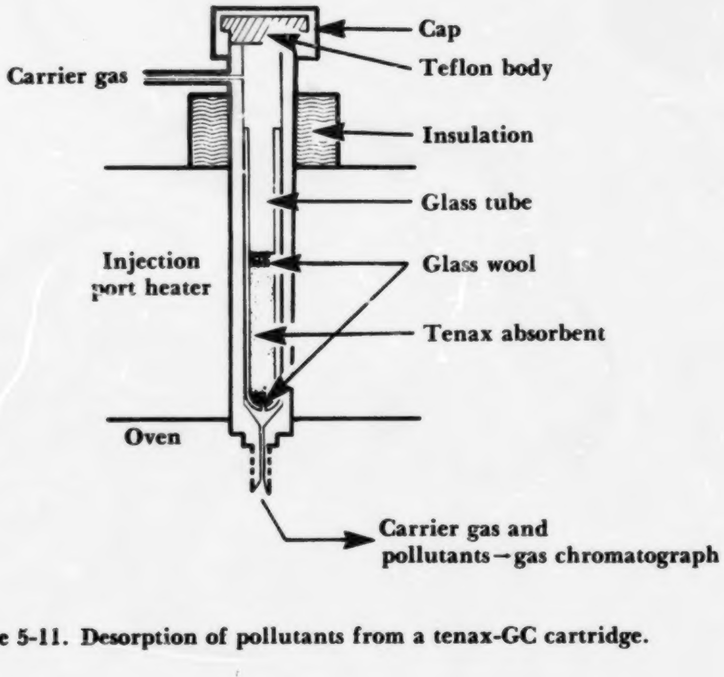
Cap
Teflon body
Carrier gas
Insulation
Glass tube
Injection
port heater
Glass wool
Tenax absorbent
Oven
Carrier gas and
pollutants→gas chromatograph

Figure 5-11. Desorption of pollutants from a tenax-GC cartridge.

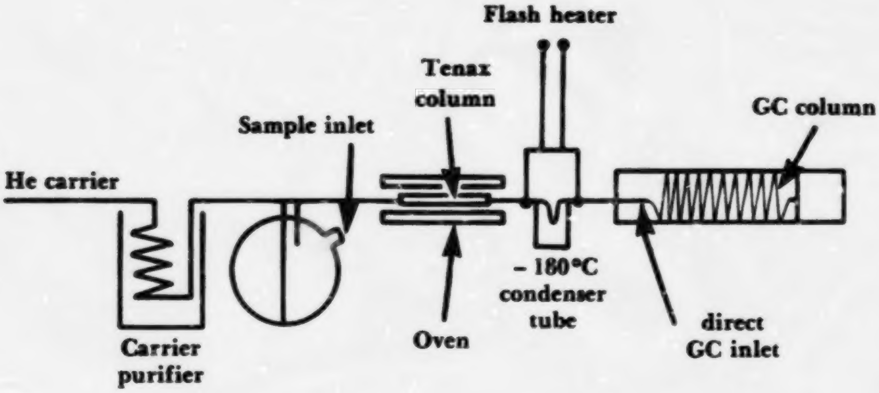
Flash heater
Tenax column
GC column
Sample inlet
He carrier
- 180°C condenser tube
direct GC inlet
Carrier purifier
Oven

Figure 5-12. Dynamic enrichment on adsorption column (experimental set-up).

Summary

The adsorption process is characterized by either physical or chemical forces. In some cases both types may be involved. Where physical forces predominate the process is termed physical adsorption, whereas chemical adsorption describes chemical action.

Adsorption phenomena may be quantitated by considering such adsorbate-adsorbent characteristics as gas composition, concentration, and temperature, as well as adsorbent type, surface area, and pore size.

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Selection and Performance of Wet Collector Media

Introduction

In the design of sampling trains, the most important component of the entire system is the collector. The process of pollutant removal is generally accomplished by absorption, adsorption, etc. The collector may take the form of a bubbler, impinger, etc. The process to be discussed is that using a wet collector for the collection of gases, vapors, and particulate matter. Some of the more important factors to consider are:

- Gas flow rate
- Bubble size
- Height of liquid column
- Reaction rate
- Solubility of pollutant

Absorber Design

General Considerations

Solubility of Pollutant

The solubility of a pollutant in a solvent must be considered in determining the type of absorber to choose. It will also determine the conditions under which the sample will be taken. The absorption coefficient is one method employed to express the results of solubility measurements with gases. The absorption coefficient α is given by:

(Eq. 5-7)

$$\alpha = \frac{V_o}{(V)(p)}$$

Where:

V_o = *the volume of gas dissolved (ml)*
V = *the volume of solvent (ml)*
p = *the partial pressure of the gas (atm.)*

Some typical absorption coefficients are given in Figure 5-13.

Solvent	H_2	He	N_2	O_2	CO	CO_2	NO	H_2S	NH_3
Water	.017	.009	.015	.028	.025	.88	.047	2.68	710
Carbon disulfide	.031	—	.049	—	.076	.83	—	—	—
Chloroform	—	—	.120	.205	.177	3.45	—	—	—
Ethyl alcohol	.080	.028	.130	.143	.177	3.0	—	—	—
Acetone	.065	.030	.129	.207	.198	6.5	—	—	—
Ethyl ether	.12	—	.24	.415	.38	5.0	—	—	—
Benzene	.066	.018	.104	.163	.153	—	—	—	—

(Glasstone, S., Textbook of Physical Chemistry, p. 695, D. Van Nostrand, New York, 1946)

Figure 5-13. Absorption coefficient of gases at 20°C.

Influence of temperature—When gases dissolve in a liquid, there is generally a liberation of heat; it follows, therefore, that an increase of temperature will result in a decrease of solubility. It is for this reason that gases may be readily expelled from solution by boiling. By thermodynamic methods, it is possible to show that an increase in temperature will decrease the solubility of a gas. This effect can be seen in Figure 5-14.

Gas/temp	Helium	Nitrogen	Oxygen	Carbon dioxide
0C	.0094	.0235	.0489	1.713
30C	.0081	.0134	.0261	.665

(Glasstone, S., Textbook of Physical Chemistry, p. 696).

Figure 5-14. Influence of temperature on solubilities of gases in water.

Influence of pressure—The most important factor influencing the solubility of a gas is pressure; increasing the pressure of the gas will tend to increase its solubility. The pressure is expressed by Henry's law, which states that the mass of a gas dissolved by a given volume of solvent, at constant temperature is proportional to the pressure of the gas which it is in equilibrium.

(Eq. 5-9) $$m = kp$$

Where:
m = *mass of gas dissolved by unit volume of solvent (g)*
p = *equilibrium pressure (atm.)*
k = *constant*

Some examples of pressure versus solubility effects are given in Figure 5-15.

Solvent/pressure	Methyl alcohol	Acetone	Methyl acetate
100mm	42.5	67.2	75.8
200mm	42.7	68.0	77.1
400mm	43.1	69.2	77.6
700mm	43.3	72.8	79.0

(Glasstone, S., Textbook of Physical Chemistry, p. 697).

Figure 5-15. Influence of pressure on solubility of CO_2 in various solvents at -59°C.

Rate of Reaction

All chemical reactions take place at a definite rate, depending on process conditions. The most important factors are: concentration of reactants, temperature, and presence of a catalyst or inhibitor. Some reactions are so rapid that they appear to be instantaneous, whereas others are so slow at ordinary temperatures that no detectable change would be observed in the course of years. Between these two extremes are many processes taking place with measurable velocities at temperatures easily accessible in the laboratory.

Since the rate of a reaction is proportional to the concentration of the reacting substances it is evident that the rate of the process must fall off as the reaction proceeds. This phenomenon can, however, be used to advantage by increasing the concentration of the absorbing liquid, thereby forcing the reaction to approach completion rapidly.

Collection Efficiency

There are three major factors inherent in the design of a bubbler that can affect the efficiency of the absorber.

- Flow rate
- Bubble size
- Height of liquid column

Bubble Size

The surface area at the gas-liquid interface is inversely related to the average volume of the gas bubble. As the volume of individual bubbles decreases, the surface area at the gas-liquid interface increases.

The efficiency of absorption of a gas or vapor by chemical reaction or physical absorption depends on the probability of successful collisions with molecules of reagent or solvent at the gas-liquid interface. For a given concentration of reagent this will depend on the surface area of the gas bubbles, on the length of the column of liquid through which the bubbles must pass, and the rate at which they rise through the liquid.

Collection efficiency varies inversely with flow rate and bubble size and varies directly with the height of the liquid column.

Flowrate

The gas flow rate through an absorber is one of the factors determining the efficiency of an absorber. Figure 5-16 shows clearly that as flow rate increases, for the absorbers studied, the efficiency decreases. This efficiency versus flow rate curve should be determined for each absorber and used in any analysis.

Height of Liquid Column

The length of the column of liquid in an absorber is important in determining efficiency. The velocity of rise of bubbles is approximately constant at 24 cm./sec. for bubble diameters greater than 0.2 cm (7). Since the bubbles rise at approximately 24 cm./sec. they will be in contact with a liquid column 24 cm. long for 1 second, 48 cm. long for 2 seconds, etc. *The longer the gas bubble is in contact with the liquid, the more pollutant is transferred* from the gas phase to the liquid phase until gas-liquid equilibrium is approached.

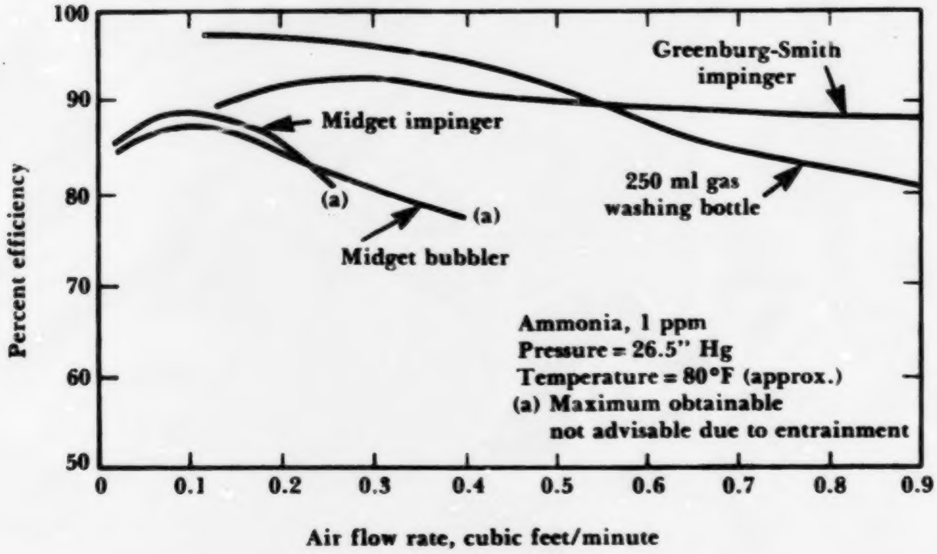

Figure 5-16. Performance curves—commercially available absorbers.

Retention of Gases and Vapors by Solution

The equation defining Raoults' Law is:

(Eq. 5-10) $$p = Np_o$$

Where:
p = *partial pressure of gas to be dissolved (atm.)*
N = *mole fraction of gas*
p_o = *vapor pressure of gas (atm.)*

From this relationship one can calculate the solubility of a gas below its critical temperature, on the assumption that the solution behaves in an ideal manner. For example, the critical temperature of ethane is 34 °C. At 25 °C the pure liquid has a vapor pressure of 42 atmospheres. According to Raoult's Law, therefore, the solubility of ethane at 25 °C and a pressure of 1 atm. in any solvent in mole fraction can be determined by the following:

$$N = \frac{p}{p_o} = \frac{1}{42} = 0.024$$

since p is 1 atm., and p_o is 42 atm. The actual solubility in n-hexane at 25 °C and 1 atm. pressure is 0.017 mole fraction. This variation is due to n-hexane being a non-ideal solvent.

To extend the method for calculating gaseous solubilities to temperatures above the critical temperature, it is necessary to estimate the hypothetical vapor pressure of the liquid by a suitable extrapolation. This is best done by using the integrated form of the Clapeyron-Clausius equation, which is,

(Eq. 5-11)

$$\log \frac{p_2}{p_1} = \frac{L_v}{4.576} \left[\frac{T_2 - T_1}{T_2 T_1} \right]$$

where L_v is the latent heat of vaporization.

If the vapor pressure at any two temperatures is known, the value at any other temperature may be evaluated on the assumption that the molar heat of vaporation remains constant. The critical temperature of methane is 95.5°C, and the hypothetical vapor pressure of the liquid at 20°C is 310 atm., giving an ideal solubility at this temperature and a pressure of 1 atm. of $1/310 = 0.0032$ mole fraction; this is very close to the solubilities actually found in n-hexane and m-xylene. Since the solubility in mole fractions of a gas at 1 atm. pressure is equal to $1/p$, where p is the vapor pressure of the liquified gas, it is evident that, for ideal solutions, the lower the vapor pressure at the given temperature the greater will be the solubility of the gas. Gases that are liquified only with difficulty, that is to say, those having very low boiling points, may be regarded as having high vapor pressures; such gases will, therefore, have low solubilities. *It follows that, in general, easily liquifiable gases will be the most soluble; this is in agreement with observation in most cases.*

Although the solubility of a gas, in mole fractions, should theoretically be independent of the nature of the solvent, this is not true in practice because of departure from ideal behavior. Some data for solutions of gases, showing deviations, are listed in Figure 5-17. The solubilities in water are exceptionally low, since water is both polar and associated, and also has a very high internal pressure, solutions of gases of the type mentioned in Figure 5-17 would hardly be expected to behave ideally. Even chlorine and carbon dioxide, which interact with water and are generally regarded as relatively soluble gases, have solubilities considerably below the calculated values, because of their low polarity and internal pressure. A quite different type of behavior is shown by ammonia, which is a highly polar substance with a high internal pressure. In hydrocarbon solvents, therefore, solubility is considerably below the ideal value, whereas in alcohol and water the observed solubility is somewhat greater than that calculated. If allowance could be made for interaction between ammonia and the solvent, good agreement would be found. A corollary to the foregoing conclusions is that for a number of *gases of similar polarity and internal pressure (e.g., hydrogen, nitrogen, carbon monoxide, oxygen) that do not react with the solvent, the ratio of the solubilities in various solvents should be approximately independent of the nature of the gas.* This generalization is roughly true in practice, and only gases such as carbon dioxide and ammonia, which are not in the same category, are exceptions.

Gas	Ideal	Nitrobenzene	Ethyl alcohol	Aniline	Water
Nitrogen	10	2.6	3.3	1.1	0.13
Carbon dioxide	11	3.9	4.5	1.9	0.19
Oxygen	16				0.17
Argon	21		6.5		0.17

Figure 5-17. Ideal and observed solubilities at 20°C.

Retention of Gases and Vapor by Chemical Reaction

The usual objective in the selection of an absorbent for scrubbing a gas is to find a liquid, possibly a solution, with a very large capacity for absorbing the solute without building up an appreciable equilibrium back pressure. This can be accomplished readily by choosing a chemical with which the solute reacts irreversibly, as when an aqueous solution of sodium hydroxide is used to absorb carbon dioxide. There are indeed very few absorptions of a gas in a liquid that are not accompanied by a chemical reaction to some degree. Thus, when ammonia dissolves in water, ionization occurs that may be looked upon as a chemical change. A similar phenomenon, though potentially weaker, occurs when carbon dioxide dissolves in water. A much stronger and more definite chemical change takes place when ammonia is dissolved in an acid, or carbon dioxide in a base.

There is no sharp line dividing pure physical absorption from absorption controlled by the rate of a chemical reaction. Most cases fall in the intermediate range; the rate of absorption being limited both by resistance to diffusion and by the finite rate of reaction. Simultaneous occurrence of a chemical reaction renders the mechanism of absorption more complicated. The theory of purely physical absorption rests on the assumption of the two-film concept. This theory may be carried over to the case where a simultaneous reaction occurs, however, modification in film resistance will become apparent. Thus when carbon dioxide is dissolved in water, the rate controlling factor is not the migration of the dissolved carbon dioxide from the liquid surface into the liquid interior, simply because the rate of solution of the gas in water is small from the very start. On the other hand if absorption of carbon dioxide in a solution of sodium hydroxide is considered, the rate of absorption is very rapid and then the rate of migration of the carbonate into the main body of the liquid becomes rate controlling.

These phenomena are complex, and, although considerable advances have been made, the situation is still very obscure. *Whenever there is a pronounced chemical reaction occurring simultaneously with absorption, there are essentially two effects that must be considered*; these pertain to:

- *Modification of capacity (rate) data*
- *Modification of the driving force.*

Capacity coefficients will generally, but not always increase when a chemical reaction occurs simultaneously with absorption. At present there is no data available to permit a correlation that will allow for estimation of capacity data.

As far as driving force is concerned, an increase is usually observed as a consequence of a chemical reaction. In many cases the dissolved gas, once having reacted with a constitutent in the liquid, offers virtually no resistance to further absorption. This is the case when carbon dioxide or sulfur dioxide are dissolved in basic solutions.

Retention of Particulate Matter

The design of the absorber plays a most important part in the retention of particulate matter by a liquid. A liquid absorber is highly efficient for retaining particles only when the velocity of the air at the jet approaches that of sound and the particles impinge with high velocity on a surface in the liquid. The sudden change in kinetic energy results in the virtually complete trapping of all particles having a diameter greater than 1 micrometer.

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Principles of Grab Sampling

Introduction

The term "grab sample" suggests two concepts: (a) a sample taken at a particular time and place within an interval of a few seconds to a minute or two, and (b) a small representative portion removed from the gross sample with no alteration.

Grab samples are usually collected in one of the following ways:

- Using an evacuated container,
- Purging (displacement of air),
- Displacement of a liquid,
- Inflation of a plastic bag,
- Using a syringe,
- Using an adsorbent cartridge.

Evacuated Containers

Evacuated containers used for grab sampling are of several types. One common type is a strong glass bulb of 250—300 ml capacity (although bulbs with volumes as large as 1—2 liters are sometimes used) (see Figure 5-18).

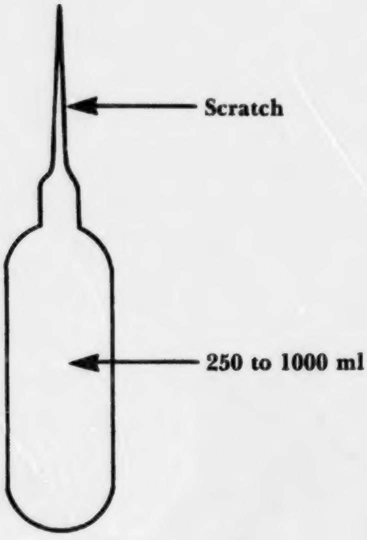

Figure 5-18. Vacuum tube.

To use this type of container, the bulb is evacuated until almost all the air has been removed. In the last stages of evacuation, the neck is sealed. Then at the sampling site, the neck is scratched and broken. Sampling is instantaneous, and will continue until the internal pressure is equivalent to the external pressure. The broken end is then sealed with wax and sent to the lab for analysis.

There are several advantages in the use of this collector: it is simple to use and no pump or manometer need be taken to the sampling site. However, the tube must be redrawn, re-evacuated and resealed if it is to be used again. There is also the danger of breakage.

An evacuated flask fitted with a stopcock or vacuum cap can also be used in this type of sampling (see Figure 5-19). The flask is evacuated and then sealed by giving the cap a half turn. When sampling is to occur, the cap is turned to the "open" position and the air will be drawn into the flask. The cap is closed after sampling and the flask is returned to the laboratory.

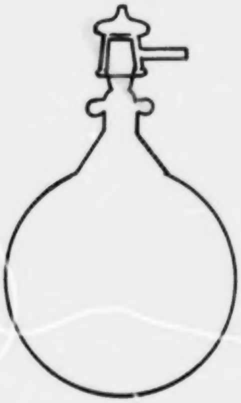

Figure 5-19. Vacuum flask.

During the transport of the evacuated container to the sampling site there is a possibility of slow leakage through poorly-fitted stopcocks. This would, of course, completely invalidate the results. The pollutants to be analyzed may also degrade or react with other compounds in the evacuated flask. This apparatus has the advantage of being easy to reuse. Such collectors should be placed in a protective container or wrapped with adhesive tape to reduce hazards of implosion.

If for some reason the containers are not completely evacuated, it may be necessary to subtract a residual volume from the volume of the flask to determine the volume of air sampled. Let V_f be the volume of the vessel; after evacuation let the temperature and residual pressure in the flask be T_1 and P_1. The flask is transported to the sampling site and opened; the flask temperature and pressure now become T_2 and P_2. The volume of air sampled, V_s, is given by:

(Eq. 5-12) $$V_s = V_f - V_x$$

Where V_x is the volume occupied by the residual gas. Assuming gas ideality for the residual gas:

(Eq. 5-13)

$$\frac{P_2 V_x}{T_2} = \frac{P_1 V_f}{T_1}$$

Hence:

$$V_x = V_f \left(1 - \frac{P_1 T_2}{P_2 T_1} \right)$$

If the ratio P_1/P_2 is small (almost complete evacuation) then the correction can be neglected and

$$V_s = V_f$$

The presence of the pollutant in the residual gas would further complicate the matter.

Air Displacement or Purging

Cylindrical tubes with stopcocks at each end are used as collectors (see Figure 5-20). The stopcocks are opened and the tube is thoroughly purged. After sampling, the tube should be held in place until the stopcocks have been closed and the aspirating device has been removed.

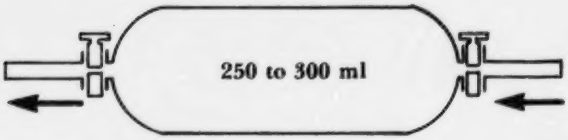

Figure 5-20. Gas-displacement collector

Metal containers of the same general design have been employed, but they have been found to react with many samples. Their real advantage lies in the fact that they are virtually unbreakable.

The sample air is drawn through the container using any of a variety of pumps. Enough air must be drawn through to completely flush out old unrepresentative air that may be present.

The necessary volume of air required will vary, but in all cases it will be at least several times greater than the volume of the container. Theoretically all of the old air can never be eliminated by pumping. Since this pumping process may take a relatively long time, it is not strictly an instantaneous sample. If the concentration of pollutant in the air changes radically during purging, the results will not necessarily be close to the average over the time interval involved.

Liquid Displacement

Another technique used in gas sampling is liquid displacement. In this method a liquid is allowed to drain from the bottom of a container, while an opening at the top allows the gas to enter and fill the space left by the liquid. Any suitable liquid that will not dissolve the sample nor react with it can be used. The choice of liquid will depend upon the material being sampled; some commonly used liquids are water, brine, mercury, or water saturated with the gas to be sampled.

Containers used are of two basic types: (a) a glass tube with two stopcocks as used in air displacement (see Figure 5-21) and (b) an aspirator bottle (see Figure 5-22).

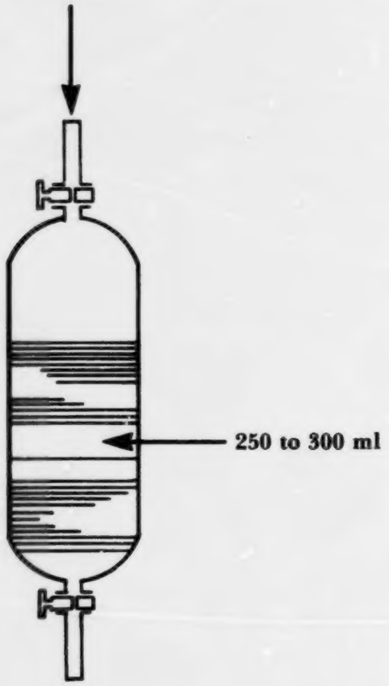

Figure 5-21. Liquid displacement collector.

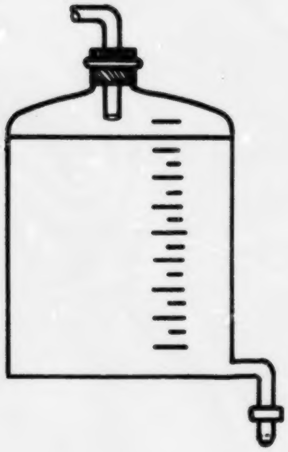

Figure 5-22. Aspirator bottle.

In both cases, the liquid is allowed to drain through the lower opening (the rate can be controlled by adjusting the stopcock) and the gas is drawn in through the upper stopcock or tube. This method requires a minimum of equipment and no special training. The container may be calibrated to indicate the volume of gas sampled.

Inflation

A fourth gas sampling method is the collection of a sample by inflation of a plastic bag (2). Plastics of various types have been used. The choice of material will depend upon the gas to be sampled and the storage period.

Some hazards to look out for in "bag sampling" are: wall effects, memory effects (where previous constituents linger), sample deterioration over time, sample deterioration due to sunlight in some cases, and the possibility of reactions among the various gases in the bag.

The deflated plastic bag is placed in a closed air tight box, with only a tube extending outside the box. An opening in the box itself is connected to a vacuum source, and the air is pumped out of the box. As the air is removed from the outer container, the bag will inflate, drawing in the sample. The air may be metered as it is pumped out of the box, thus indicating the volume of gas sample drawn into the bag (see Figure 5-23).

Syringes

Syringes may be used in the collection of small gas samples. This technique has been widely applied in the field of odor measurement.

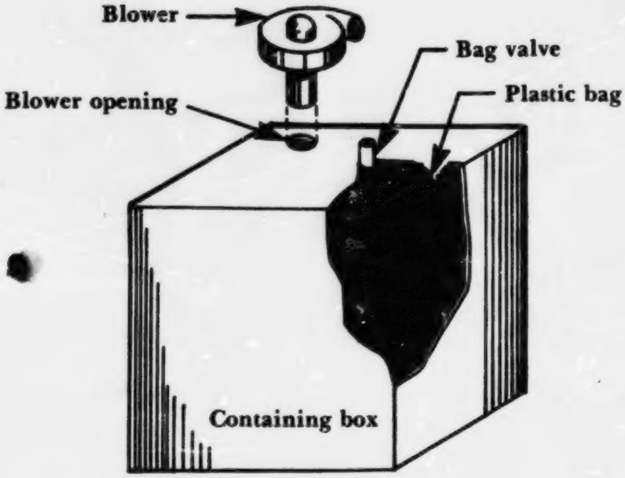

Figure 5-23. Inflation sampler.

Grab Sampling Techniques

Grab sampling techniques are preferable to continuous sampling in certain situations. Some constituents have absorption rates too slow for efficient collection by absorption. Field conditions (lack of electricity and lab facilities) often necessitate this type of sampling.

Grab sampling is useful when concentrations vary considerably over a period of time, and it is necessary to obtain a sample at a specific time. Most grab sampling techniques utilize a minimum of equipment and require little or no special training or experience on the part of the operator (5).

Grab sampling has a serious limitation – the sample obtained is generally not large enough to detect very small quantities of materials except by the most sensitive techniques.

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Principles of Freezout Sampling

Introduction

Air pollutants existing as gases can be trapped or removed by the freezout or condensation method. Trapping in this discussion refers to the mechanism of sample collection, and removed implies an air-cleaning mechanism to rid unwanted gas contaminants from the gas stream. The method has a very high efficiency at relatively low flow rates. Certain problems are encountered when using the freezeout method, thus necessitating an appraisal of the method for particular applications.

Concept

The method consists essentially of drawing air through collection chambers with progressively lower temperatures. If the temperatures of the chambers are approximately equal to or less than the boiling point (the temperature at which a liquid is converted to a gas) of the gaseous components of the air passing through it, these components will exhibit a phase change from the gaseous phase to the liquid phase. The condensate (liquid phase) is collected in the chamber where the phase change occurs. The gaseous contaminants to be collected will determine the temperatures required in the collection chambers. The temperatures of the chambers can be controlled by using different immersion bath liquids. Contaminants with boiling points as low as − 195 °C can be collected by this method.

Equipment

The type of freezeout equipment required depends to a large extent on the application. The required amount of equipment of a given type depends on whether the sampling apparatus is a single or multistage unit.

The size of the collection chamber varies according to the immersion bath for which it was designed. The collection chambers themselves are placed in Dewar flasks containing the cooling solutions (see Figure 5-24).

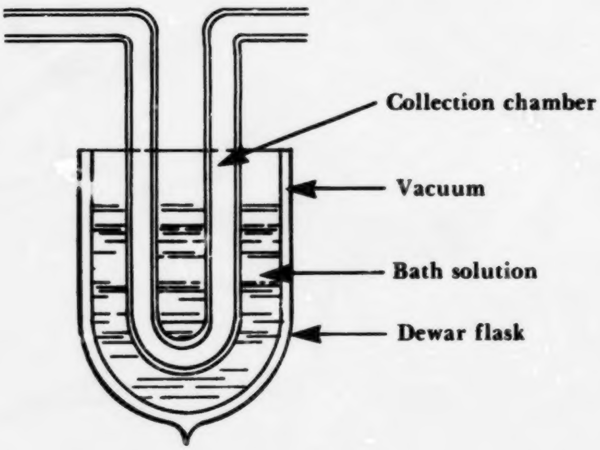

Figure 5-24. Freezeout unit.

Figure 5-25 indicates various bath solutions and some sizes of the Dewar flasks that have been used for each. The volume of the bath solutions and thus the size of the collecting chamber itself are partially due to factors such as:

- Temperature gradients across the collecting chambers as related to the criticality of the boiling point of the contaminant being collected;
- The surface area as related to the evaportation rate of the bath solution; and
- The condensation of water vapor in the primary collection chambers, thus necessitating a larger volume.

Bath solution	Temperature	Volume of solution
Ice + salt	− 16 °C	≈2 liter
Dry ice & acetone or methyl-cellosolve	− 80 °C	750 ml
Liquid oxygen	− 183 °C	100 ml
Liquid nitrogen	− 195 °C	100 ml

Figure 5-25. Bath solutions.

The level of the solutions in the baths should be kept at 2" to 4" within the top of the collection chambers in an attempt to maintain a constant temperature throughout the chamber.

Among the collection chambers utilized, U-shaped and spiral-shaped tubes are prominent. Large radius bends should be designed into the tubes to facilitate smooth airflow and to prevent ice accumulation at the bends. Freezout devices can be classified into two categories, single and multistage units.

Single-Stage Units

A single-stage unit (see Figure 5-24), consists of one collection chamber (glass or metal) immersed in a bath solution. As has already been mentioned, the temperature of the bath and consequently the liquid of the bath will depend on the particular gas to be sampled.

Multistage Units

Multistage units consist of a series of collection chambers. These chambers can be arranged in either horizontal or vertical trains (see Figure 5-26 and 5-27). In these trains the temperatures of the baths are progressively lower. This allows for condensation of different gases in different chambers.

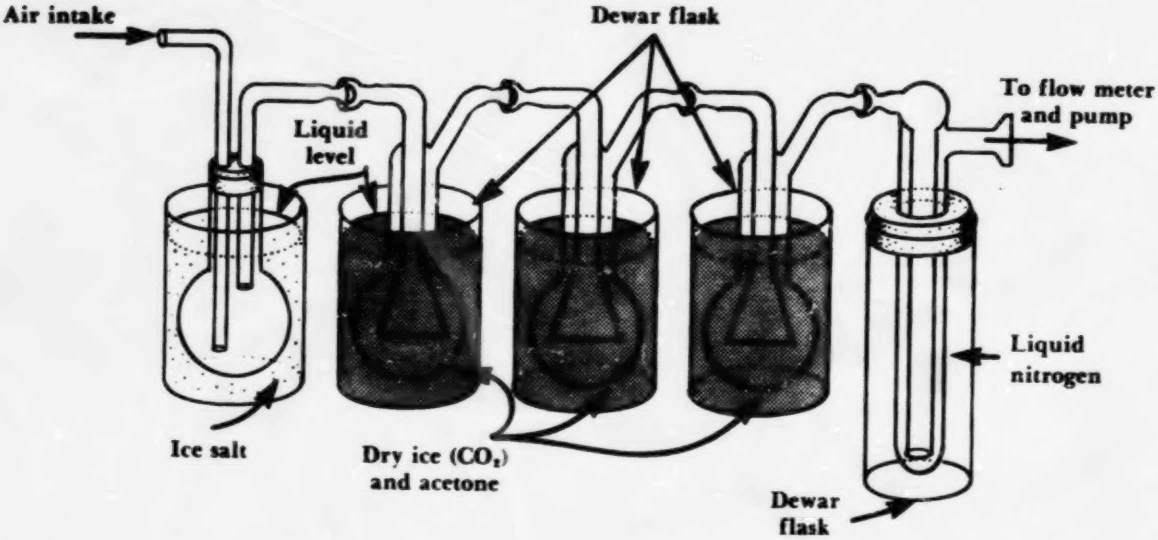
Air intake
Dewar flask
To flow meter and pump
Liquid level
Liquid nitrogen
Ice salt
Dry ice (CO$_2$) and acetone
Dewar flask

Figure 5-26. Freezeout equipment for atmospheric samples (horizontal sampling train).

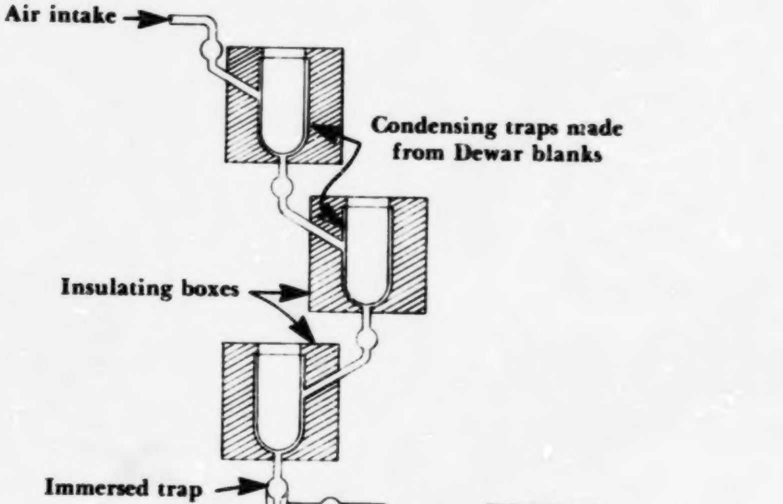
Air intake
Condensing traps made from Dewar blanks
Insulating boxes
Immersed trap
Vacuum pump

Figure 5-27. Freezeout equipment for atmospheric samples (vertical sampling train).

Efficiency

The collection efficiencies of the previously described systems are not very good. To efficiently condense gases it is necessary for the gas to come in contact with the cold surface of the collection chamber. Therefore, the efficiency of collection by freezeout can be improved by: (a) filling the collection chamber with some type of material that will increase the cold surface area and (b) reducing the flow rate.

Packing Materials

To increase the cold surface area within the collection chamber, various materials such as glass beads, metal packing (1) and activated carbon (2) have been used (see Figure 5-28). In one application, for collecting benzene and formaldehyde, the glass beads and metal packing increased the efficiency from 50% to 65% and 80%, respectively (1). The lower collection efficiency of the unpacked train was due partly to the formation of a fine mist that was not retained by the walls of the traps.

In another application using activated carbon, a collection efficiency of 100% was reported for xenon and krypton (2). The activated carbon gave a much larger surface area for the gas to pass over. The use of activated carbon will give the added advantage of adsorbing gases from the air stream.

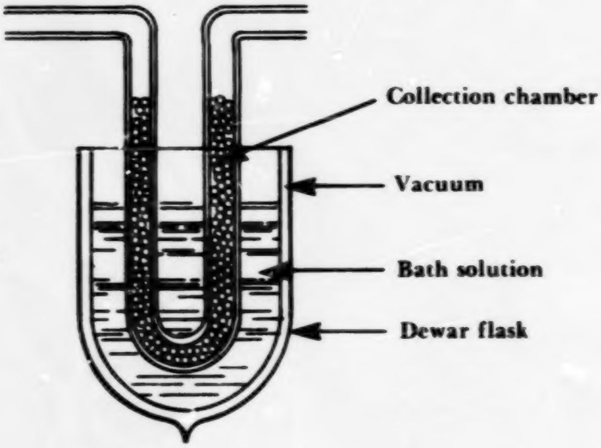

Figure 5-28. Freezeout unit showing packing material.

Flow Rate

The flow rate through the train should be such that a sufficient "detention time" (time allowed for the gas to come into equilibrium with its surrounding temperature) be available to allow the desired collection efficiency. For an unpacked train the detention time must be relatively large due to the small cold surface area. By packing the train with a surface-area-increasing material the cold surface area will increase and the detention time can become smaller. With a smaller required detention time the rate of flow through the train can be greater. Flow rates on the order of 0.1 to 0.2 cfm have been reported for unpacked trains, while 1 to 2 cfm (2) have been reported for trains packed with activated carbon.

Another factor affecting flow rate is the formation of ice crystals in the bends of the collection chambers. This will be discussed in another section.

Errors

One possible source of error is that gases soluble in water will be removed to some extent prior to their removal in a collection chamber. Other errors may be introduced when electrostatic precipitators, drying towers, etc., are placed ahead of the freezeout train. Electrostatic precipitators will aid in the removal of particulates, but they may also alter the gas chemically (1). Adsorption of vapors by a desiccant placed before the collection chamber has also been reported. This adsorption might introduce errors in the final results.

Sensitivity

The sensitivity of the freezeout method depends primarily on the gas collected, volume of air sampled, and how the collected gas is analyzed. Hydrocarbon samples were analyzed on a mass spectrometer to detect pollutant concentrations of 10^{-4} ppm from a 1 liter sample. With larger sample volumes, concentrations on the order of 10^{-6} ppm have been reported (3).

Applications

The freezeout method has proved useful in sampling gases. The freezeout device can be used as a collecting train itself, or it can be used in conjunction with other sample collection devices. Also, freezeout traps are used in the lab to concentrate trace amounts of pollutants (such as halogenated hydrocarbons) desorbed from adsorption cartridges in order to increase their detectibilities. This probably is its chief use today.

Freezeout Train

Trains composed of several collection chambers have the ability of collecting several gases at the same time. This may aid in the gross analysis of the sample because the sample will be broken into fractional parts according to the various boiling points of the gases.

Probably the main disadvantage of a freezeout train is the plugging of the collection chambers by ice crystals. Drying towers placed on the inlet side of the train will help alleviate this problem as well as filter some particulates. When drying towers are used the flow rate is dependent upon the speed at which the desiccant will help alleviate this problem as well as filter some particulates. When drying towers are used the flow rate is dependent upon the speed at which the desiccant will effectively remove the water moisture from the air. Flow rates of 1 to 2 cfm have been reported when using a drying tower (2).

Liquid oxygen creates another problem when it is used as a bath solution or when collected in a collection chamber. When used as a bath solution extreme care must be employed because of the ability of liquid oxygen to support combustion. Therefore, a restricted personnel area around the sampler must be maintained. Oxygen (B.P. = −183°C) will condense when liquid nitrogen (B.P. = −196°C) is used as a bath solution. This is undesirable since it will dilute the collected contaminants. If the solution is allowed to warm up after sampling, a portion of the contaminants may be carried off by the escaping oxygen (1).

Multicollection Train

The freezeout train may be part of a larger train where particulate filters, electrostatic precipitators, activated charcoal cartridges, etc., make up the rest of the train. The major advantage of such a train would be the removal of particulates and gases that were not of interest. Probably the main disadvantage of the larger train is the possibility of altering the chemical composition of the gas of interest.

Summary

Freezeout trains have proved to be an efficient collection device. Collection efficiencies of 100% for flow rates up to 2 cfm have been reported for certain contaminants. Problems such as water vapor condensation with subsequent plugging of collecting chambers can be alleviated by using a desiccant on the inlet side of the train. Collection efficiency improvements such as increasing the cold surface area can be accomplished by using a packing material. The use of freezeout devices for "field" operations has its limitations because of its bulkiness and the problem of keeping the bath solutions at a constant level.

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Chapter 6

Generation of Standard Test Atmospheres

Introduction

Calibration of atmospheric sampling equipment is very important for air monitoring; and it must be done to ensure that the data generated by air monitors represent the actual concentration of pollutants in air. Many factors may affect the calibration of sampling or monitoring devices, preventing them from providing a true measure of the atmospheric contaminant concentrations. The generation of standard test atmospheres is essential to the calibration procedures for continuous air monitoring instrumentation.

There is a need for reliable, accurate methods to generate pollutant gases of known concentration. For example, an air monitor may be designed to operate at a certain efficiency, but due to factors such as reagent deterioration, electrical or electronic component variability, and flow rate changes, data generated by an air monitor may differ from the true concentration of a pollutant in air. To evaluate the performance of sampling equipment, known contaminant concentrations must be introduced; by knowing the input concentration, the output of the monitor can be determined for accuracy and a function generated showing the relationship between the input concentration and output instrument response. The purpose of this section is to discuss the methods of preparing gases of known concentration.

The most important factor in the preparation of these standard atmospheres is devising a method of preparing gases of known concentration. Moreover, in the preparation of the standard atmospheres, devising a method of creating accurate calibration gases at the extremely small concentrations typically found in the atmosphere is often difficult. Many methods are now available for creating gases in high concentrations, but atmospheric testing often requires concentrations in the sub part-per-million range.

Static Systems

Pressurized Systems

Although pressurized tanks of known contaminant concentrations are usually purchased, they may be prepared by the following procedures. Cylinders containing a pollutant gas are prepared by adding a known volume of pollutant gas and then pressurizing the cylinder with a diluent gas. The gas is then of known concentration and can be used for calibration purposes. The range of concentrations that

can be achieved by this method are typically less than 100 ppm to more than 5000 ppm, depending on the stability of the gaseous pollutant. The concentration of the mixture can be calculated as follows:

(Eq. 6-1)

$$c_{ppm} = \frac{10^6 \times V_c}{V_d + V_c} = \frac{10^6 p_c}{p_t}$$

or

(Eq. 6-2)

$$c_{\%} = \frac{10^2 \times V_c}{V_d + V_c} = \frac{10^2 p_c}{p_t}$$

Where:

c_{ppm} = ***concentration of gas mixture, ppm by volume***
$c_{\%}$ = ***concentration of gas mixture, percent***
V_c = *volume of contaminant gas*
V_d = *volume of diluent gases*
p_c = *partial pressure of contaminant gas*
p_t = *total pressure of the gas mixture*

Using the rigid container procedure it is necessary to construct a gas-handling manifold that interconnects the vacuum source, the calibrated volume, the source of contaminant gas, and the gas cylinder. Subsequently, the entire system is evacuated; the known calibration volume is flushed and filled at atmospheric pressure with the contaminant gas and isolated, and connecting lines are again evacuated. The contaminant gas is then swept by diluent carrier gas into the cylinder; and the cylinder pressurized with diluent gas to the desired pressure. Because of compressional heating the cylinder should be allowed to equilibrate at room temperature before reading the pressure to be used in the concentration calculations. The concentration of the mixture is calculated as follows:

(Eq. 6-3)

$$c_{ppm} = \frac{10^6 \times V_c \times P_b}{V_{cyl} \times P_t}$$

Where:

c_{ppm} = ***concentration of mixture, ppm by volume***
V_c = *volume of pure contaminant gas*
V_{cyl} = ***volume of cylinder***
P_b = ***barometric pressure at time of filling***
P_t = *final total pressure of cylinder*

One factor that must be watched closely when preparing gas mixtures by this method is the thoroughness of the mixing. When introducing the gases into the cylinder one at a time, a layering effect may occur and result in incomplete mixing. This effect can be counteracted by allowing for adequate mixing time before use.

It should be noted that at room temperature and pressure most gas mixtures conform closely to the ideal gas law. However, at the higher pressures that are present in the cylinders, gaseous mixtures can deviate from this law and create errors of up to 20%. This can be corrected by using a quantity called the compressibility factor (K). The units for the pressure and volume are not important as long as P_c and P_t are in the same units and V_c and V_d are in the same units since both parts-per-million and percent are unitless quantities.

In commercial practice, compressed gas cylinders of calibration gases are often prepared using high load mass balances: in this procedure, a precise tare weight for an evacuated cylinder is obtained, and the cylinder is weighed again following the addition of the desired trace constituent and after the addition of the diluent gas (prepurified nitrogen in most cases) under pressure. The mass fraction of the contaminant gas is converted to a volumetric concentration by application of the usual formula involving molecular weight and molar volume.

When prepared by the user, a pressure dilution technique of some sort is generally necessary. Here the volume of the contaminant gas introduced, V_c, the volume of the cylinder, V_{cyl}, the evacuation pressure, P_{evac}, and the final total pressure in the cylinder P_t must be known.

Using this procedure the cylinder is evacuated using a vacuum pump capable of producing a very low pressure. Depending upon the exact capacity of the pump, the previous contents and size of the cylinder, and the final pressure to be used, the evacuation pressure may be ignored in the calculations. For example, if the cylinder was evacuated to a few torrs and the final pressure was 30 atmospheres the calculation error in ignoring the evacuation pressure, i.e., assuming it is zero, would only be about 1 part in 10,000.

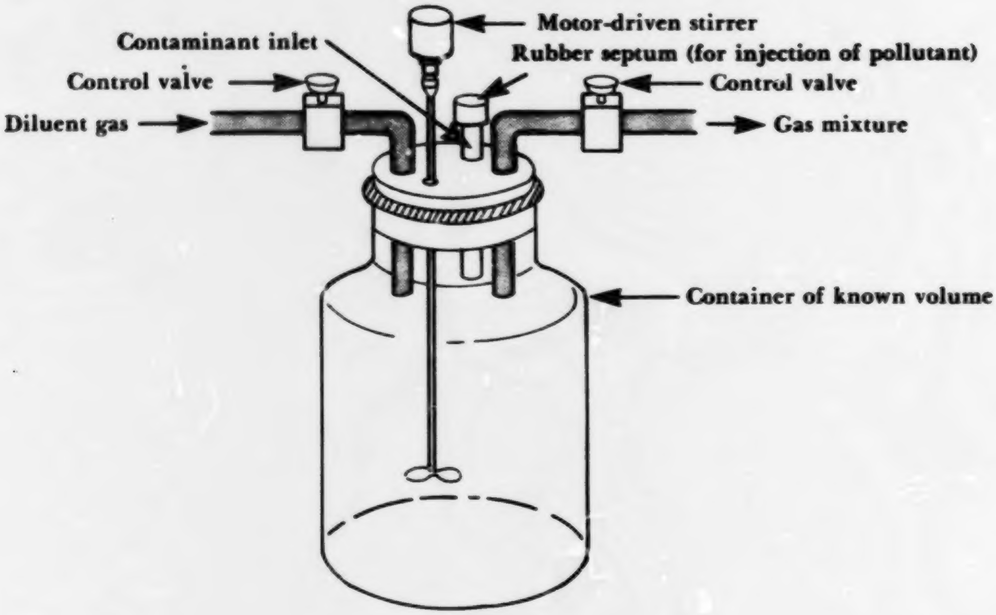
As a matter of good practice, cylinders should be continued in the same service and not interchanged; for example, a cylinder formerly used for SO_2 span gas should not be converted to NO_2 service. Further, cylinder materials consistent with the gases to be contained therein should be used.

Following the evacuation of the cylinder the contaminant gas is introduced using a syringe technique, as described in the bag procedure, or using a small rigid container of precisely known volume.

Rigid Chambers

Rigid chambers such as the one illustrated in Figure 6-1 (1) are another method of preparing an analytical gas standard.

The gaseous contaminant is introduced into the vessel, mixed with the diluent gas, and sampled. The volume of the chamber may vary with the type of application but the principle remains the same. Preparation of standard gas mixtures by this procedure has been largely replaced by more accurate permeation devices and pressurized cylinders containing a specified pollutant concentration.



Motor-driven stirrer
Contaminant inlet
Rubber septum (for injection of pollutant)
Control valve
Control valve
Diluent gas
Gas mixture
Container of known volume

Figure 6-1. Rigid chamber used for producing standard gas mixture.

Nonrigid Chambers—Bag Samples

In this procedure, a bag, usually of a flexible nonreactive plastic material, is filled with a known volume of diluent gas, and a known volume of contaminant gas is added to the system. The diluent gas should be cleaned of all interfering constituents and be nonreactive to the desired contaminant. After allowing for complete mixing in the bag, a sample can be drawn off for calibration purposes. The concentration of contaminant in the bag mixture can be calculated by (if the initial contaminant concentration is 100%):

(Eq. 6-4)

$$c = \frac{V_c}{V_d + V_c}$$

Where:

c = *concentration of diluted contaminant, ppm by volume*

V_c = *volume of contaminant gas,* $\mu\ell$

V_d = *volume of diluent gas,* ℓ

One of the first and most important steps in this preparation is the selection of the bag. The bag must be of a flexible material and be chemically inert to the gases it will contain. Chemical inertness is very important; if the contaminant gas reacts with the bag, the amount of contaminant will decrease and the actual concentration of the bag mixture will be unknown. Teflon, Mylar and copolymer Tedlar bags have been widely used because they are inert to most materials. Before any bag is to be used, it should be tested with the contaminant gas to be sure that no reaction will take place between the bag and the gas. After the bag has been selected, it should be checked for leaks before the sample is introduced; particularly the seams of the bag and the area around the valve. The bag should be flushed and evacuated at least three times to ensure that all unwanted contaminants have been removed. The actual filling of the bag must be done under controlled conditions to guarantee measurement of the volume. Clean air is pumped into the bag through an accurately calibrated flowmeter. The flow rate of the diluent gas must be kept as constant as possible throughout the filling procedure to obtain an accurate measure of volume. After the flow rate is set, a stopwatch is used to get an accurate filling time. The product of the flow rate and the filling time is the total volume of diluent gas added to the system.

The contaminant sample should be introduced into the stream of diluent gas as the bag is filling. This should be done after the bag has filled about one-quarter of the desired volume. By introducing the sample at this time, mixing can take place as the bag fills to its final volume. The sample is introduced into the diluent gas stream with the use of a syringe. A rubber septum and tee assembly is located in the filling line for insertion of the syringe. Care must be used when handling the syringe to ensure that the desired quantity of contaminant is introduced.

The syringe should have a graduated barrel so that the amount of contaminant entered can be read directly. The plunger of the syringe must be gas tight so no sample will escape while being injected into the diluent gas stream. A Teflon cap can be fitted over the plunger to eliminate gas escaping during introduction. The sample gas is extracted with the syringe from a source of known concentration. When drawing the sample, the syringe should be filled and evacuated at least six times with the sample gas to eliminate any air that may have been present in the needle. The plunger of the syringe should be drawn well past the desired volume when entering the sample. Just before introducing the sample into the diluent gas stream, the syringe should be adjusted to the desired volume to eliminate any error from air that may have diffused into the needle. Care should be taken in handling the syringe; it should never be held by the barrel or the needle (2). Heat from the hand of an analyst will cause the gas in the syringe to expand and part of the sample will be lost from the needle. When introducing the sample, the tip of the needle should be in the middle of the diluent gas stream to prevent the sample from being lost on the walls of the filling lines. After depressing the plunger, remove the needle from the gas stream immediately to ensure that none of the sample will diffuse out of the needle and into the gas stream, giving a higher resulting concentration. Mixing time can be decreased by kneading the bag for several minutes.

The concentration of the calibrated gas will change during storage. The decay rate will depend upon the substance being stored, the relative humidity, and the bag material. Substances such as nitrogen dioxide and ozone will decay faster than carbon monoxide and hydrocarbons. Figure 6-2 (1) illustrates the rate of decay with time of a known concentration of SO_2 stored in a bag. The decay rate can be decreased if the bag is preconditioned. The preconditioning requires that the bag be flushed several times with the sample gas. The bag should be left overnight at least once with a sample gas in it as a preconditioning step.

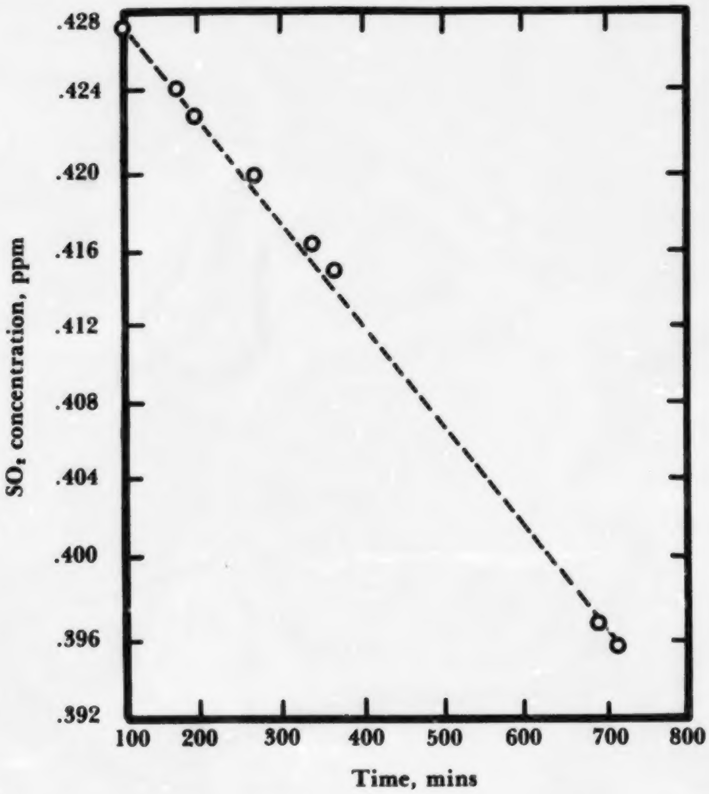


Figure 6-2. Rate of decay of SO_2 concentration in a bag.

It should be noted that the bag-filling method is only an approximate method of preparing a known gas mixture concentration. A reference method should be used to determine the actual concentration of the bag mixture.

Polasek et al. (2) found that sample stability depends clearly on the compound and type of bag material used. Figure 6-3 gives the results of carbon monoxide deterioration with time in bags of various materials.

Bag material	**pvc**	**Tedlar**	**Snout***	**Aluminized polyester**
No. of bags tested	10	10	5	3
Concn of calibration gas used to fill bags, ppm	9.0	9.0	8.2	8.2
O h after filling, av ppm	8.9	8.5	8.2	8.0
Av deviation, ppm	− 0.12	− 0.5	0	−0.17
Av sqd deviation, ppm²	0.056	0.352	0.012	0.030
24 h after filling, av ppm	8.5	7.5	8.0	7.9
Av deviation, ppm	− 0.50	− 1.5	−0.16	−0.30
Av sqd deviation, ppm²	0.306	4.2	0.048	0.097
48 h after filling, av ppm	8.4	6.8	8.3	8.2
Av deviation, ppm	− 0.63	− 2.2	0.10	−0.03
Av sqd deviation, ppm²	0.497	7.7	0.010	0.010
100 h after filling, av ppm	7.9	5.2	8.0	7.7
Av deviation, ppm	− 1.2	− 3.8	−0.18	−0.50
Av sqd deviation, ppm²	1.5	17.8	0.066	0.25

*Consists of layers of polyester, polyvinyl chloride, aluminum, polyamide, and polyethylene.

Figure 6-3. Carbon monoxide sample deterioration with time in bags of various materials.

Dynamic Systems

Permeation Systems

The use of permeation techniques for preparation of standard mixtures is very useful for some contaminants. The method is based on the theory that a gas confined above its liquified form at a constant temperature will permeate through some materials at a constant rate. By putting a liquified gas into a Teflon tube, for example, permeation of the vapor through the tube will take place because of the concentration gradient that exists between the inner and outer tube walls. By passing different flows of diluent gas over the tube, gases of varying concentration can be generated.

The actual concentration of a sample gas can be calculated by Equation 6-5 (1).

(Eq. 6-5)

$$c = \frac{(PR)\left(\frac{24.46\mu\ell/\mu\text{-}mole}{(M)\ \mu g/\mu\text{-}mole}\right)\left(\frac{T°K}{298°K}\right)\left(\frac{760\ \text{mm Hg}}{P\ \text{mm Hg}}\right)}{Q\ \ell/\text{min}}$$

Where: *c = concentration, $\mu\ell/\ell$ or ppm by volume*
T = temperature of the system, °K
P = pressure of the system, mm Hg
PR = permeation rate, μg/min
Q = total flow rate, liters/min
M = molecular weight of the permeating gas, $\mu g/\mu$-mole
24.46 = molar volume ($\overline{V}$) of any gas at 25°C & 760 mm Hg, $\mu\ell/\mu$-mole

Permeation tubes allow for the generation of gases with concentrations in the sub-part-per-million range.

Permeation tubes are made from a variety of different materials. The material must allow the diffusion of the contaminant gas through the walls and also be inert to the diffusing gas. If some reaction took place between the tube material and the gas, the permeation rate would be affected and might no longer be constant. Teflon, Mylar, and Saran Wrap are materials often used because of their chemical inertness and good permeation properties. Before any material is used for the permeation tube, it should be tested to ensure that no changes will occur in the material when it comes in contact with liquified gas. To test the material, a piece should be placed in some of the liquified gas it will contain. The material should be removed after a few days and checked to see if any changes in the material have occurred (i.e. brittleness, holes, stickiness, etc.). If there are no apparent changes, the material is probably suitable for use.

The first step in the construction of the tube is to compress the desired sample gas to a liquid state. The liquified gas is then put into a tube and the tube ends are sealed. One method of sealing the tube ends is to force glass beads or stainless steel balls into the tube ends. To seal properly, these beads should be approximately one and one-half times the inside diameter of the tubes. Once the tubes have been prepared, they should be stored for two to three days in order to equilibrate. Since the permeation rate is extremely dependent upon temperature and relative humidity, the permeation tubes should be stored at a constant temperature and zero humidity. After the waiting period has ended, the tubes should be weighed on an analytical balance and replaced in the storage area. Time required to weigh the tube should be minimized and kept constant to compensate for the effects of moisture absorption. High humidity will cause the permeation tube to absorb moisture thereby increasing the tube weight. This will yield an erroneously low value for the permeation rate. Absorbed moisture on the tube can form acids that may cause tube blistering, thus changing the permeation rate. The tube should be stored and weighed several times to yield enough data to demonstrate that the permeation rate is constant. The results of these weighings should be plotted on a graph as weight versus time.

From the slope of the resulting best "fit" line, the permeation rate can be calculated in micrograms per minute as shown in Figure 6-4. The permeation rate for a particular material and sample is usually given as nanograms per minute per centimeter of the tube length.

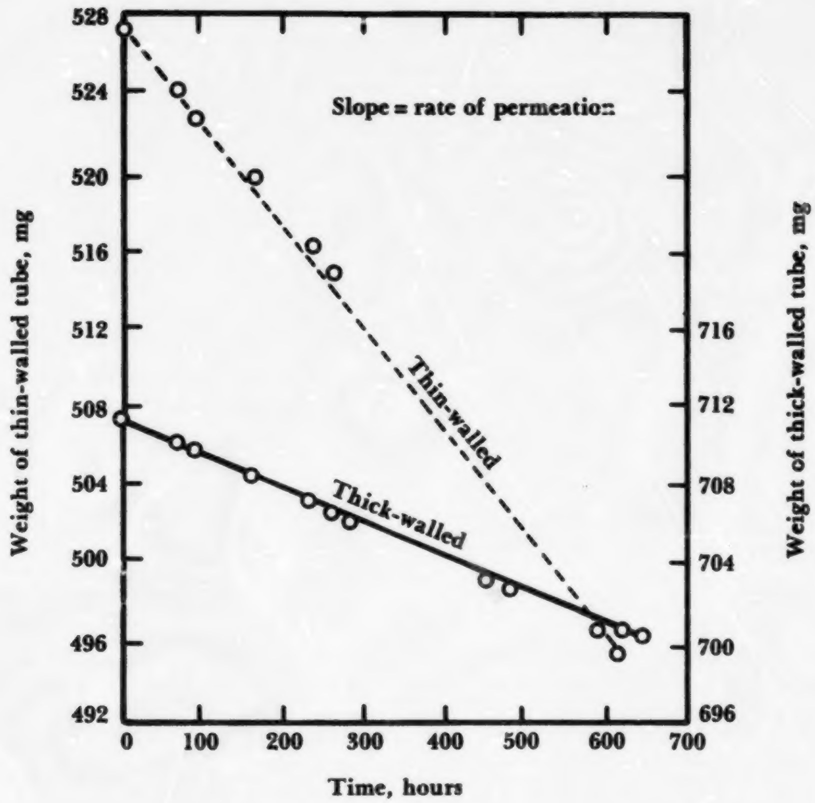


Figure 6-4. Calibration of two permeation tubes.

Once the tube has been calibrated, it can be used to generate test gases of known concentration. The permeation tube is placed in a stream of diluent gas. The gas passes over the tube and the permeated gas is mixed into the gas stream. The desired concentration can be varied by varying the flow rate of the diluent gas or by varying the permeation tube length. The diluent gas must be kept at a constant temperature during the time the calibration gas is being generated to be sure the permeation rate is constant. The temperature dependence of the permeation rate is illustrated for four gases in Figure 6-5. To accomplish this, the diluent gas is drawn through a constant temperature chamber before passing over the tube as in Figure 6-6. Permeation tubes are commercially available from many sources offering a variety of precalibrated tubes with different permeation rates. The National Bureau of Standards offers some reference sources. Figure 6-7 lists permeation rates for a number of compounds through a Teflon film. A number of configurations other than the original tube design are also commercially available. Some of these are designed to provide a longer useful life. Figure 6-8 lists some materials used to construct a permeation tube.

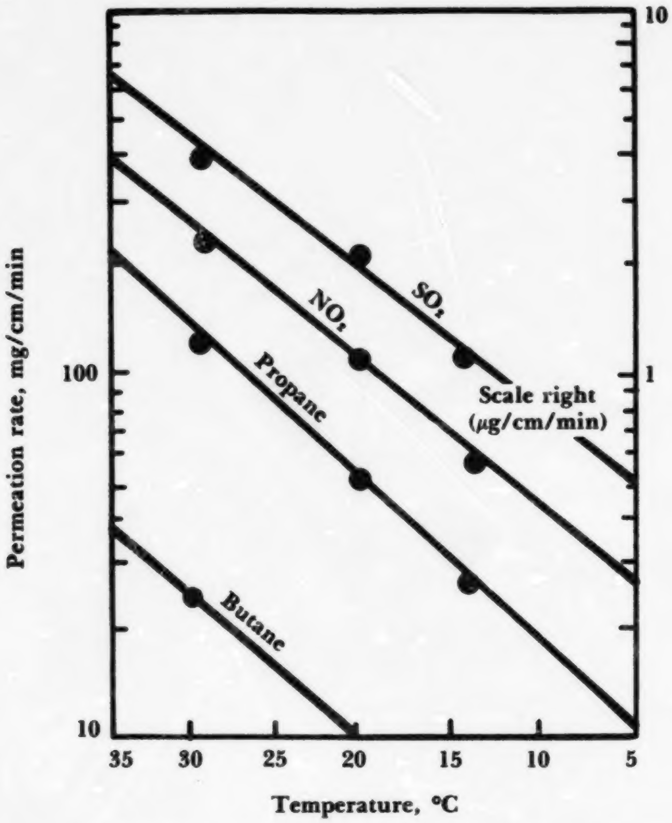


Figure 6-5. Permeation rate vs. temperature for four gases.

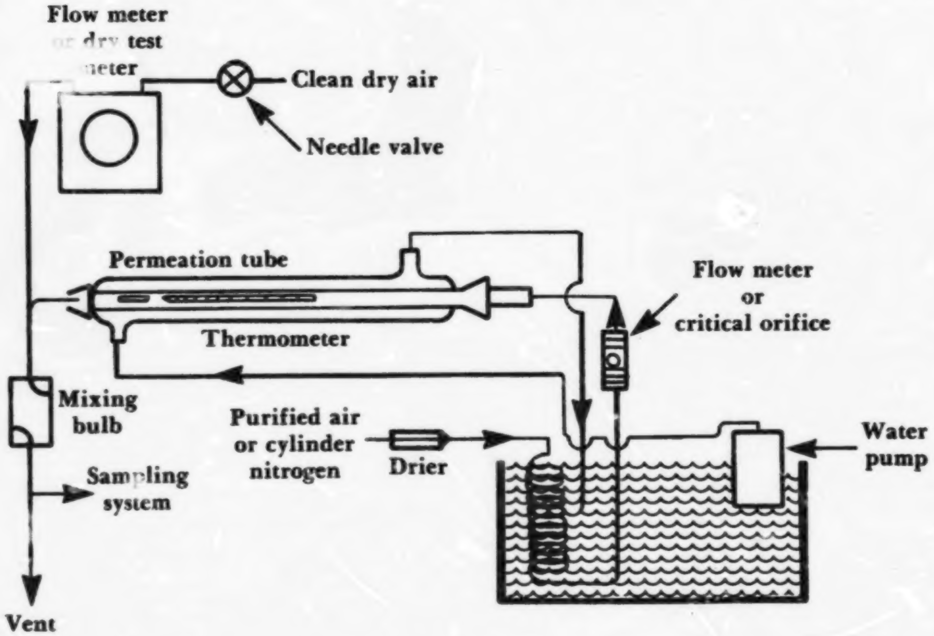

Flow meter
or dry test
meter
Clean dry air
Needle valve
Permeation tube
Thermometer
Flow meter
or
critical orifice
Mixing
bulb
Purified air
or cylinder
nitrogen
Drier
Water
pump
Sampling
system
Vent

Figure 6-6. Components and flow of a typical permeation system.

	[illegible]kness [illegible]	Temperature (°C)	Permeation rate (ng/cm/min)
	[illegible]	[illegible]0 ± 0.5	213
	[illegible]	20 ± 0.5	138
		20.1	203
		29.1	396
	[illegible]2	[illegible]3.8	605
	0[illegible]12	[illegible]1.1	1110
	[illegible]	29.1	2290
	[illegible]	[illegible]1.1	53
	[illegible]2	[illegible]9.1	119
	[illegible]	[illegible]	6.4
	[illegible]2	[illegible]	22.3
[illegible]	[illegible]	[illegible]0	2.8
[illegible]	[illegible]	93	1.3
	[illegible]	[illegible]	0.29
[illegible]	0.016	[illegible]3	0.065
$C_6H_5CH_3$	0.030	20	0.00006

Figure 6-7. Permeation rates of some typical compounds through FEP Teflon.

	Trade name
[illegible]	[illegible] Teflon
[illegible]	Alathon
[illegible]	
[illegible]ide	Saran Wrap
	Nylon 6
	Mylar
[illegible]phthalate	Mylar
	Diothene

[illegible]aterials used to construct a permeation tube.

The performance of a permeation device depends on the polymer films used to construct these tubes and the pollutant for which a standard concentration is needed. The important factors to be considered in the use of a permeation device are temperature, humidity, gas stability, equilibration time, etc. These parameters have been studied for nitrogen dioxide (3), sulfur dioxide (5), and recently for numerous halogenated hydrocarbons (5), and recently for permeation tubes constructed with FEP (fluorinated ethylene propylene copolymer) Teflon. In the case of nitrogen dioxide, the permeation device demonstrating the greatest stability and utility in terms of equilibration time and lifetime is illustrated in Figure 6-9.

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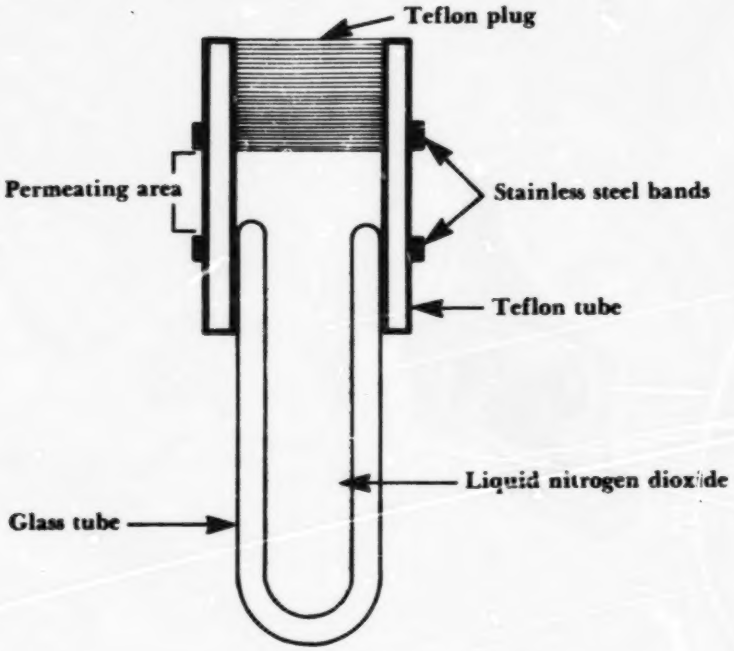
Teflon plug
Permeating area
Stainless steel bands
Teflon tube
Liquid nitrogen dioxide
Glass tube

Figure 6-9. Nitrogen dioxide permeation device.

Experimental results indicated that a small permeating area of Teflon was required for NO_2 due to the rapid permeation rate of NO_2 through the Teflon wall. Tubes constructed as in Figure 6-9 have a useable lifetime of up to 2 years (3). In contrast, the permeation rate of sulfur dioxide through the same Teflon wall is considerably slower. Permeation tubes containing this pollutant are constructed as shown in Figure 6-10.

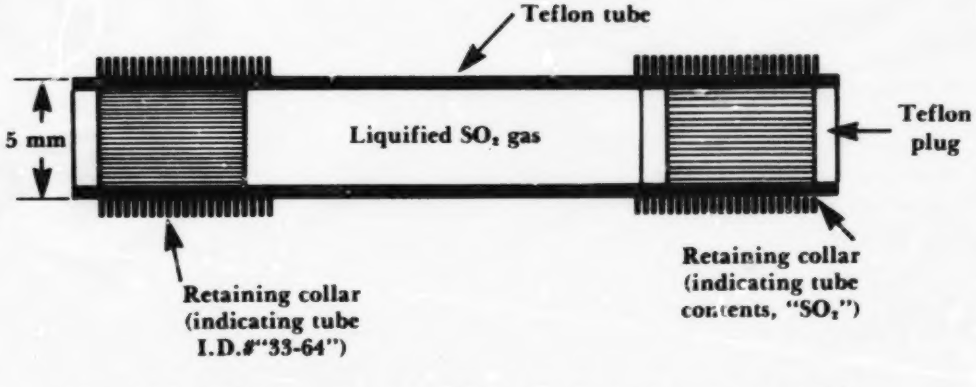
Teflon tube
5 mm
Liquified SO₂ gas
Teflon plug
Retaining collar (indicating tube I.D.#"33-64")
Retaining collar (indicating tube contents, "SO₂")

Figure 6-10. SO_2 permeation tube (NBS—standard reference material).

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To determine the rate of permeation in this type of device, the tube may simply be removed from the permeation system and weighed to the nearest 0.1 mg on an analytical balance. Generally weighings can be made daily, weekly, or monthly depending on the gas and type of permeation device. As indicated previously, the permeation rate can be determined by measuring the slope of the least-squares error line used to fit the weight vs. time data. A more rapid calibration, however, can be obtained by using the apparatus shown in Figure 6-11.

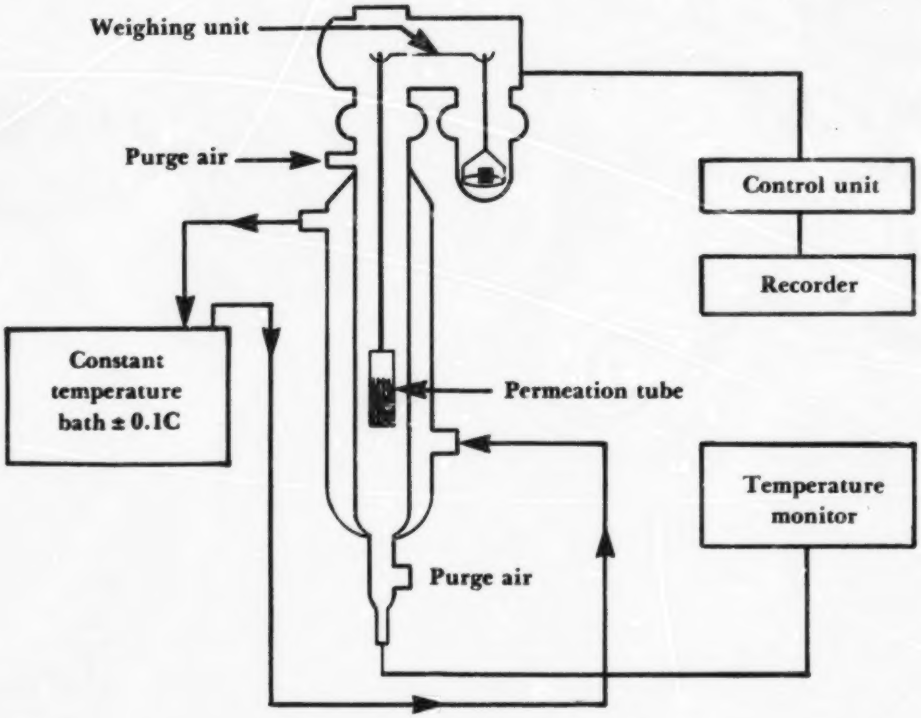
Weighing unit
Purge air
Control unit
Recorder
Constant temperature bath ± 0.1C
Permeation tube
Temperature monitor
Purge air

Figure 6-11. Gravimetric calibration apparatus.

In addition to rapid calibration, this apparatus has the advantage of continuous direct read-out of weight change (see Figure 6-12), and the permeation tube is maintained in the constant temperature bath at all times. The potential problem of spurious weight increase due to the hygroscopic nature of some pollutants (e.g., SO_2, NO_2) is eliminated with this device for the tube need never have to leave the constant temperature bath.

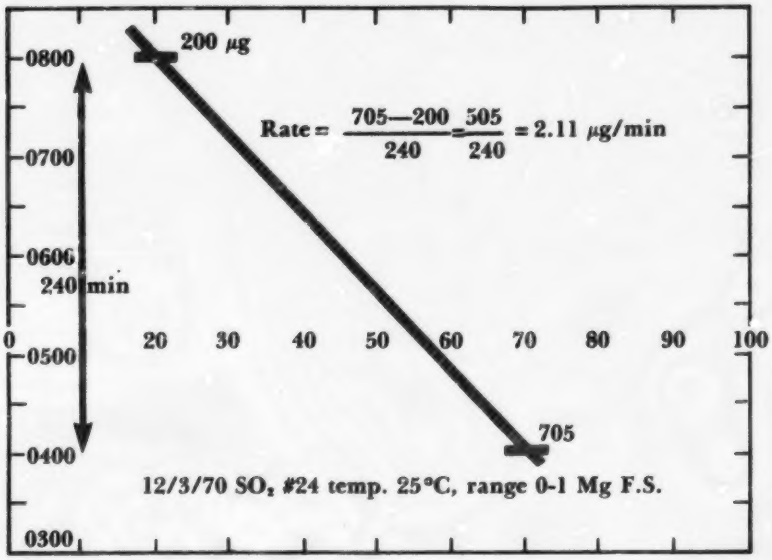

Figure 6-12. Typical stripchart read-out from an in situ gravimetric apparatus.

Dilution Systems

Single Dilution

A simple system for diluting gas entails mixing the gas with the diluent in a mixing chamber after measuring their flow rates. A single dilution system using rotameters to measure flow is illustrated in Figure 6-13 (1). The concentration of the test mixture can be calculated with the following formula:

(Eq. 6-6)

$$c_uQ_u = c_d(Q_u + Q_d)$$

$$\frac{c_uQ_u}{(Q_u + Q_d)} = c_d$$

Where:
c_u = *concentration of undiluted contaminant gas*
c_d = *concentration of diluted test mixture*
Q_u = *flow of undiluted contaminant gas*
Q_d = *flow of diluent gas*

Flow measuring devices other than rotameters are frequently used to increase the accuracy and precision of the test mixture concentration.

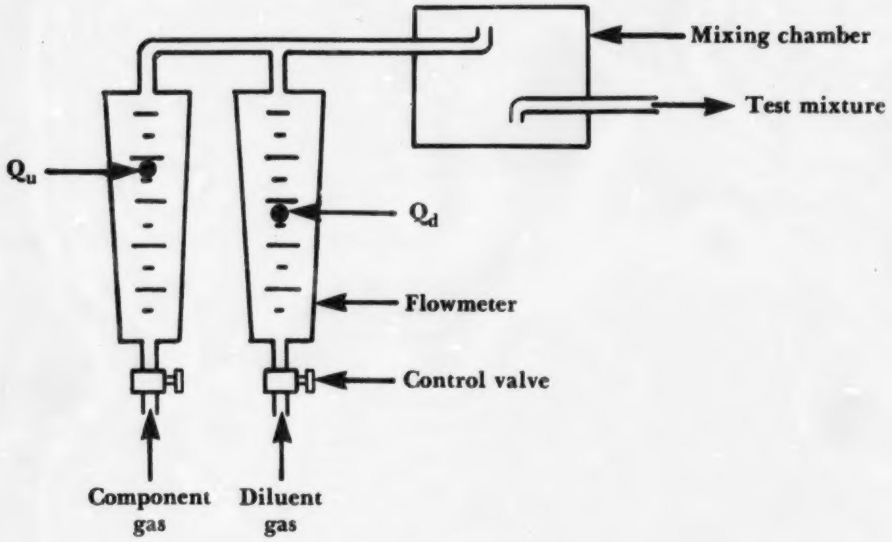

Figure 6-13. Single dilution system.

Multiple Dilution

Low-level concentrations of pollutants may be obtained by a multiple dilution system. A system such as that shown in Figure 6-14 for a double dilution avoids high dilution ratios and the use of low flow rotameters. Other methods for measuring and controlling flow (i.e., orifices, mass flowmeters, etc.) in a multiple dilution system provide a variety of means for constructing multiple dilution systems. The test mixture concentration can be calculated with the following equation:

(Eq. 6-7)

$$c_{tm} = \frac{\left(\dfrac{c_u Q_u}{Q_u + Q_{d1}}\right) Q_m}{Q_m + Q_{d2}}$$

Where (see Figure 6-14):

Q_u = *flow of undiluted contaminant gas*
Q_{d1} = *flow of first diluent gas*
Q_m = *flow of first diluent mixture*
Q_{d2} = *flow of second diluent gas*
c_u = *concentration of undiluted contaminant gas*
c_{tm} = *concentration final test mixture*

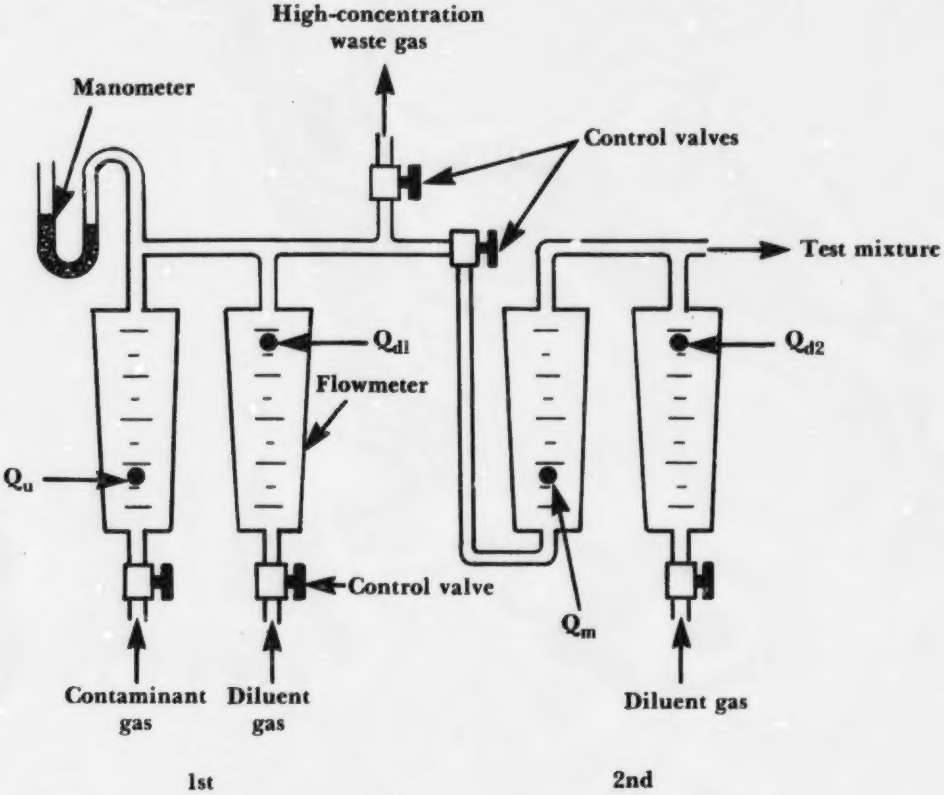

Figure 6-14. Sketch of a system for making double dilutions.

Ozone Generation

Ozone is unlike most of the gaseous pollutants in that there are no gaseous calibration standards available. This is due to ozone's instability, which makes it impossible to produce gas cylinders of standardized ozone concentrations or ozone permeation tubes. The only means available for the calibration of ozone monitors is to produce stable, known amounts of ozone at the site of calibration.

Ozone is most commonly produced by irradiating oxygen with an ultraviolet light source in an ozone generator. An ozone generator may utilize a tubular quartz chamber into which ozone-free air is admitted at a controlled, constant rate. This incoming air (from a zero air source) is subjected to ultraviolet radiation from a mercury vapor lamp.

The mercury vapor lamp is housed within an aluminum shield which can be adjusted to expose a selected portion of the lamp, thereby controlling the amount of ultraviolet radiation to which the air stream is exposed. In this way varying amounts of ozone can be produced by simply moving the shield to a number of positions across the mercury lamp. Using a pressure regulator to assure a stable flow through the generator plus a constant line source transformer to assure constant voltage to the UV lamp, the ozone generator can be expected to give stable ozone concentrations which vary by no more than ± 10 parts per billion.

Varying concentrations of ozone can also be obtained by dilution of a stable ozone source (from an ozone generator) with varying amounts of zero air (ozone-free air). One or more of the dilution techniques previously mentioned can be employed.

Evaporative Systems

Gases may be introduced into a test atmosphere by injection of the gas in the liquid phase into the moving diluent gas stream. Figures 6-15 through 6-17 exemplify several types of systems for introducing a liquified gas into a system that will produce an atmosphere of known concentrations.

Careful consideration should be given to the specific pollutant and the type of injection used. For example, syringe injection of nitrogen dioxide into a bag through a rubber septum is unadvisable since nitrogen dioxide will react with the rubber giving rise to spurious concentrations.

The approximate concentration of the test mixture can be calculated with the following formula.

(Eq. 6-8)

$$c = \frac{Q_\ell \varrho_\ell \bar{V} 10^6}{(M) Q_d}$$

Where:

c = *concentration of test mixture, in ppm*
Q_ℓ = *flow of liquid contaminant, in mℓ/min*
ϱ_ℓ = *density of liquid, in g/mℓ*
$\bar{V}$ = *molar volume of ideal gas at operating temperature and pressure in ℓ/mole*
M = *molecular weight of contaminant, in g/gm-mole*
Q_d = *flow of diluent gas, in ℓ/min.*
10^6 = *conversion to ppm*

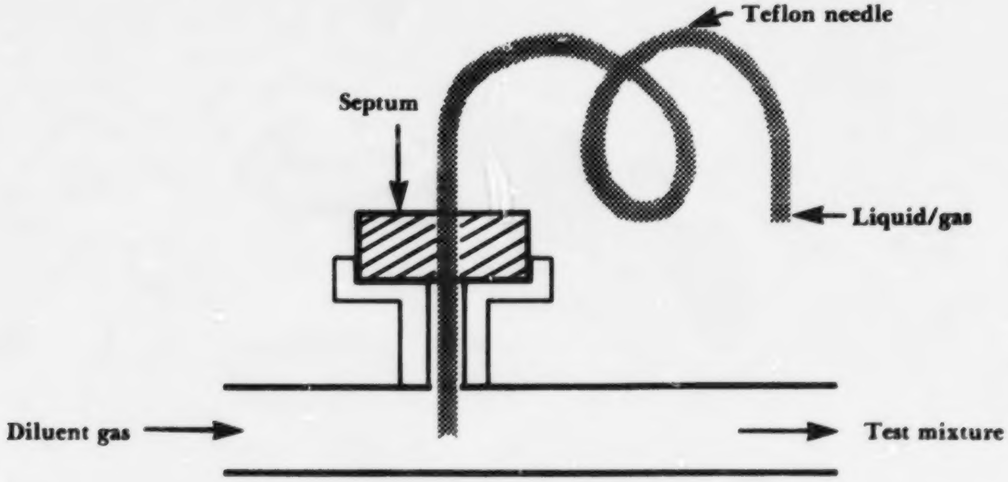

Figure 6-15. Method for injecting liquids and gases into a test atmosphere.

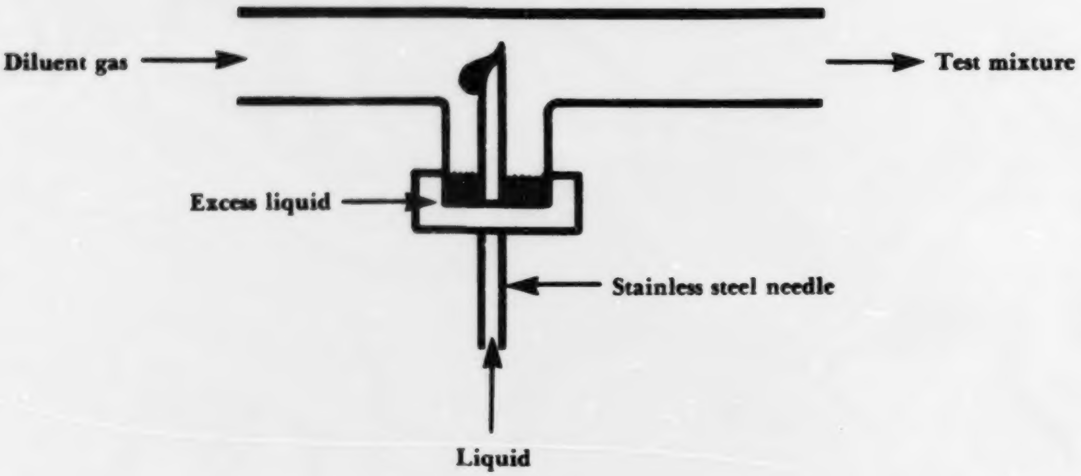
Diluent gas
Test mixture
Excess liquid
Stainless steel needle
Liquid

Figure 6-16. Method for injecting liquids into a test atmosphere.

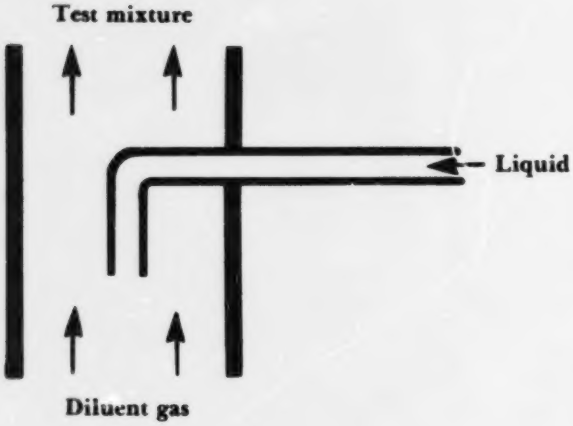
Test mixture
Liquid
Diluent gas

Figure 6-17. Method for injecting liquids into a test atmosphere.

References

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Preparation of Zero Air

Introduction

Zero air can be defined as air that is free of contaminants and interferences for a particular analysis technique (9). It is important to note that a zero air for one analysis may not be a zero air for another analysis. For example, an analysis technique may require a zero air that has only sulfur dioxide and water vapor removed while another analysis technique may call for only hydrocarbons to be removed.

Zero gases are used extensively in atmospheric sampling both in laboratory and field applications. Many continuous monitors require a constant supply of zero air for parallel path reference cells. Cylinder air can be used, but by applying the proper adsorption or absorption column on the inlet gas stream, zero gas can be continuously produced from atmospheric air. This can cut costs and eliminate the necessity of replenishing zero air cylinders. The contaminants and their typical concentrations found in clean, dry ambient air are summarized in Figure 6-18.

		Content	
Component	**Formula**	**% by Vol.**	**ppm**
Nitrogen	N_2	78.09	780,900
Oxygen	O_2	20.94	209,400
Argon	Ar	0.93	9,300
Carbon dioxide	CO_2	0.033	330
Neon	Ne	18×10^{-4}	18
Helium	He	5.2×10^{-4}	5.2
Methane	CH_4	1.5×10^{-4}	1.5
Krypton	Kr	1.0×10^{-4}	1.0
Hydrogen	H_2	0.5×10^{-4}	0.5
Nitrous oxide	N_2O	0.5×10^{-4}	0.5
Xenon	Xe	0.08×10^{-4}	0.08
Ozone*	O_3	0.03×10^{-4}	0.03
Ammonia	NH_3	0.01×10^{-4}	0.01
Iodine	I_2	0.01×10^{-4}	0.01
Nitrogen dioxide	NO_2	0.001×10^{-4}	0.001
Sulfur dioxide	SO_2	0.0002×10^{-4}	0.0002
Carbon monoxide	CO	0 to trace	—

*Ozone content in winter is 0.02 ppm and in summer is 0.03.

Figure 6-18. typical composition of clean, dry air near sea level.

There are many techniques for producing zero air. The purpose of this section is to discuss the most widely used methods for removing contaminants from a gas stream to produce a zero air. It should be noted that water vapor is a contaminant that must be removed from many gas streams. This is especially true when introducing a gas stream into a permeation tube system where the gas must be free from water vapor. This ensures proper permeation through the walls of the permeation tube (11, 12). For this reason, a separate discussion of drying a gas stream is provided in this section.

Gaseous Contaminant Removal

There are many ways of removing a gaseous contaminant from a gas stream, including the use of catalytic devices, adsorption, and absorption. Figure 6-19 lists the more commonly used materials.

Material	**Purpose**	**Preparation**
1. Activated charcoal (6 × 16 mesh)	Removes many gases such as ozone, SO_2, NO_2, higher molecular weight organic vapors. Does not remove CO, CO_2.	Commercially activated coconut hull charcoal 6 × 16 mesh.[a] Place in 2 inch I.D. × 18 inch long section of plastic pipe. Use glass wool plugs to retain charcoal in place. Plastic pipe caps on each end of cylinder are drilled and threaded to accept standard ½ inch O.D. tube fittings. Containers of other materials and similar configuration and volume may be used.
2. NO oxidizer (a) Chromium trioxide (CrO_3)	Converts NO to NO_2 for subsequent removal with TEA or soda lime[d].	Soak firebrick or alumina 15-40 mesh in a solution containing 16 g CrO_3 in 100 ml of water. Drain, dry in an oven at 105-115 °C for 30 to 60 minutes and cool. Spread a thin layer of the dry pellets in a dish and place in a desiccator containing a saturated salt solution which maintains the relative humidity (RH) between 50 to 70%. The reddish color changes to a golden orange when equilibrated. Place in a ½ inch I.D. × 15 inch glass tube. Use glass wool plugs to hold pellets in place. (Caution: protect eyes and skin when handling this material. Do not breathe oxidizer dust.) Before using, pass air containing 30 to 70% RH through the oxidizer for about 1 hour at 0.5 ℓ/min to condition. Discard when more than ¾ of the oxidizer bed depth turns brown.
(b) Humidifier	Furnishes water vapor for proper operation of oxidizer.	Pass dilute NO air stream over water at a fixed temperature such that the humidity of the air stream is maintained within 50 ± 20% RH

3. Triethanolamine (TEA)	Removes NO_2	Soak firebrick 10-20 mesh in a 20% aqueous solution of TEA. Drain, spread on a dish and dry for 30 to 60 min at 95 °C. Pellets should be free-flowing. Place in a ½ inch O.D. (7/16 inch I.D.) × 15 inch long polyethylene or stainless steel tube with standard ½ inch O.D. tube fittings on each end. Use glass wool plugs to hold the pellets in place.
4. Desiccant	Remove water	Commercial 6 × 16 mesh silica gel with color indicator.[b] Place in 3 inch I.D. × 24 inch long clear plastic cylinder capped at both ends. Caps are drilled and threaded to accommodate standard ½ inch O.D. tube fittings. Use glass wool to hold granules in place. When the change in color exceeds ¾ of the desiccant bed depth, regenerate by exposing the silica gel to 120 °C atmosphere overnight.
5. Carbon monoxide Oxidizer (Hopcalite)	Catalytically oxidize CO to CO_2 for subsequent removal with Ascarite or soda lime.	Commercial mixture of copper and manganese oxides[c]. Place granules in a ½ inch O.D. (7/16 inch I.D.) × 15 inch long section of copper pipe with standard ½ inch O.D. tube fittings on each end. Use glass wool to hold granules in place.
6. CO_2 Absorber	Remove CO_2, H_2O	a. Soda lime[d]: commercial preparation calcium and sodium hydroxides; 4 to 8 mesh. b. Ascarite[e]: a commercial preparation of sodium hydroxide in an asbestos matrix, 8-30 mesh. Place soda lime or ascarite in a 2 inch I.D. × 15 inch long section of plastic pipe. Plastic caps at both ends are drilled and threaded to accept standard ½ inch O.D. tube fittings.

[a] Activated coconut hull charcoal, Type PCB 6 × 16 mesh, Pittsburgh Activated Charcoal, Merk & Co., Inc. Pittsburgh, PA 15230

[b] Silica gel, indicating, 6 × 16 mesh, Grace Davison Chemical, Baltimore, MD 21226

[c] Carbon monoxide purifier, (Hopcalite) Model RAF-BCHDI, Robbins, Aviation, Inc., Vernon, CA 90058

[d] Soda lime, 4-8 mesh, J. T. Baker Chemical Co., Phillipsburg, NJ 08865

[e] Ascarite, 8-30 mesh, ibid.

Figure 6-19. Materials used in producing zero air up to 30 ℓ/min.

Catalytic Devices

Catalytic devices have been used to selectively remove a gas from the sample stream. This leaves a reference or zero gas that is minus only the pollutant to be measured. Using this method, the change in output when the catalyst bed is bypassed will be due only to the pollutant measured. An example of a specialized catalytic conversion is the UV absorption ozone monitor. Ozone is selectively removed from the sample using a manganese dioxide catalyst that reduces ozone to oxygen (1, 2). This ozone-free sample, which still contains all other gases, is the reference or zero air for the UV ozone monitor and is used as the baseline. The gas stream then bypasses the catalyst, and the ozone-carrying gas enters the monitor where the change in output can be attributed specifically to the ozone.

Adsorption

Adsorption is a widely used method for removing contaminants from a gas stream to form a reference or zero air. Solid adsorbents have the ability to adsorb quantities of gases because they have extremely high surface areas per unit weight, e.g., activated carbon has a surface area ranging from 300 to 1400 m^2/gm (18). A more detailed discussion of the porous quality of adsorbents may be found in the literature (3, 8, 18). Figure 6-20 lists the properties of some common adsorbents.

Adsorbent	Form	External surface Area, ft^2/lb	Pore volume ft^3/lb	Reactivation Temp, °F	Max. gas flow, CFH/lb	Sp. heat, C_p Btu/(lb°R)	Typical Adsorbates
Activated carbon	Pellets	10.5 - 21.5	0.010 - 0.013	200 - 1000	/	0.25	CH_4 through
	Beads (G)	15.0 - 24.0		200 - 1000	/	0.25	n-C_5H_{12}, CO_2, H_2S
Silica gel	Beads (G)	5.0 - 16.0	0.007	250 - 450	75	0.22	CH_4 through
	Beads (S)	6.0		300 - 450	75	0.25	C_4H_{10}, C_2H_4 through C_4H_8. H_2O, H_2S, SO_2
Activated alumina	Beads (G)	7.0 - 18.5	0.006	350 - 600	50	0.22	H_2O, H_2S
	Beads (S)	4.0 - 8.0		350 - 1000	50	0.25	Oil vapors
Molecular sieves	Pellets	9.0 - 14.5	/	300 - 600	/	0.23	See Figs. 6-22 6-23
	Beads (G)	32.0	/	300 - 600	/	0.23	6-24
	Beads (S)	7.5 - 12.5	/	300 - 600	/	0.23	

G = Granules
S = Spheroids

Figure 6-20. Typical properties of adsorbents.

Activated carbon and molecular sieves are the most widely used solid adsorbents for the removal of contaminants. Activated carbon has been used extensively for the adsorption of many contaminant gases in a sample stream not only in atmospheric sampling and in laboratory use but also as an industrial adsorbent in continuous flowing adsorption towers (16). The term "activated" carbon derives from a method of enhancing the adsorption properties of regular carbon. The carbon is "activated" by heating at 900°C in a reducing atmosphere to increase the porous nature of the carbon thereby increasing the adsorbency of the carbon (4).

Activated carbon can be made from many substances including soft coal, fruit pits, nut shells, and coconut shells. Coconut shell carbon is the desired form of activated carbon because of its porous nature. Figure 6-21 lists the adsorptive capacity of activated carbon for several gases.

Gas	Volume adsorbed, cm^3
SO_2	380
CH_3Cl	277
NH_3	181
H_2S	99
HCl	72
C_2H_2	49
CO_2	48
CH_4	16
CO	9
O_2	8
N_2	8
H_2	5

Figure 6-21. Adsorption of gases by carbon (1 gm of adsorbent, temperature 15°C).

Molecular sieves are also widely used as adsorbents because of their porous nature. The molecular sieves are usually made from synthetic zeolite crystals or metal aluminosilicates. The diameter of the pores or passageways of the molecular sieve regulates the size of the molecules that may pass through the sieve. Because of this, molecular sieves have been used extensively in the fractionation of organic gases (hydrocarbons) as packing material in gas chromatographic columns. Various properties of molecular sieves are summarized in Figures 6-22, 6-23, and 6-24.

Adsorbed on 4A & 5A molecular sieve	Adsorbed on 5A but not 4A molecular sieve	Not adsorbed on 5A or 4A molecular sieve
Water CO_2 CO* H_2S SO_2 NH_3 NO_2* O_2* CH_4* Methanol Ethane Ethylene Acetylene Propylene n-Propanol Ethylene Oxide	Propane and higher n-paraffins to C_{14} Butene and higher n-olefins n-Butanol and higher n-alcohols Cyclopropane Freon 12	Isobutane and all iso-paraffins Isopropanol and all iso, sec and tert-alcohols Benzene and all aromatics Cyclohexane and all cyclics with at least 4 numbered rings Carbon Tetrachloride Sulfur Hexafluoride Hexachlorobutadiene Freon 114 and 11 Boron Trifluoride Molecules larger than 5 Å

*Adsorbed below −20°F

Figure 6-22. Molecular sieve adsorption characteristics.

	Nominal pore diameter, μ	Molecules adsorbed*	Remarks
3A	0.003	< 3 Å effective diameter (e.g. H_2O, NH_3)	Used for drying and dehydration
4A	0.004	< 4 Å diameter (e.g. H_2S, Ethanol, CO_2, SO_2, C_2H_4 & C_2H_6)	Scavenge water from solvents and sat. hydrocarbons (HC).
5A	0.005	< 5 Å diameter (e.g. n-C_4H_9-OH n-C_4H_{10}, C_3H_8 to $C_{22}H_{46}$)	Separates n-paraffins from branched & cyclic HC.
10X	0.008	< 8 Å diameter (e.g. iso-paraffin & olefins, C_6H_6)	Separates aromatic HC.
13X	0.010	< 10 Å diameter	Drying, H_2S & mercaptan removal (gas sweetening)

*Each type adsorbs listed molecules plus those of preceding types

Figure 6-23. Molecular sieves—Linde type.

Zeolite	Amount sorbed @ 25°C (g/100g of molecular sieve)		
	H_2O	n-C_6H_{14}	Cyclohexane
4A	24.5	—	—
5A	24.5	12.0	—
B	20.0	—	—
X	31.5	16.8	18.5
Y	28.0	16.5	19.0
Erionite	11.3	4.4	6.7
Offretite	16.6	8.6	5.3
Mordentite	13.3	6.1	7.3

Figure 6-24. Effective sorption capacities of molecular sieves.

Acid gases in the atmosphere can prove to be interferences for analytical and continuous monitoring techniques. An often used adsorbent for these gases is Ascarite. This strongly basic adsorbent, 91% NaOH, will remove acid gases from the sample stream. Ascarite has also been used extensively for selectively removing carbon dioxide from a gas stream (17).

Absorption

Absorption is also a means of removing unwanted gases from the sample stream. One absorptive method could be much like the sampling of gases through impingers: the contaminant could be scrubbed from the system using a liquid solution. Solid absorbents are also used. Levaggi et al. (7) discuss a method of absorbing nitrogen dioxide from a gas stream by using triethanolamine on firebrick. This will selectively absorb nitrogen dioxide while allowing the passage of nitric oxide.

Water Vapor Removal

As mentioned previously, water vapor removal is very important in the preparation of calibration gases using permeation tubes. Water vapor removal is also important when using some catalysts or adsorbents. For example, water vapor must be removed before passing a gas stream over a bed of Hopcalite, because water vapor causes Hopcalite to lose its oxidizing properties (19). There are many other situations where water vapor must be removed. The three most widely used laboratory and air sampling methods of removing water vapor (drying) from a gas stream are adsorption, absorption, and condensation.

Adsorption

Adsorption of water vapor on solid desiccants is the most common method of drying a gas stream. This is because solid desiccants are readily available, easy to handle and store, can be regenerated, and can be prepared with an indicator material in them that changes color when the desiccant is spent.

The choice of a drying agent should not be based solely on its drying ability. Other factors, such as stability, temperature dependency, ability to perform in high humidity situations, emission of gases through reaction with the moisture, etc. should be taken into account.

The three most widely used drying adsorbents are silica gel, calcium sulfate, and anhydrous magnesium perchlorate. Efficiency and capacities of these and other solid desiccants are listed in Figures 6-25 and 6-26.

Material	Volume of air per hr. per ml. desiccant, ml	Total vol. of air per ml. of desiccant, liters	Residual water vapor per liter of air, mg
$CuSO_4$ (anhy)	36 to 50	0.45 to 0.7	2.8 (2.7 to 2.9)
$CaCl_2$ (gran.)	66 to 165	6.1 to 24.2	1.5 (1.4 to 1.6)
$CaCl_2$ (tech. anhy.)	115 to 150	4.0 to 5.8	1.25 (1.23-1.27)
$ZnCl_2$ (sticks)	120 to 335	0.8 to 2.1	0.98 (0.94-1.02)
$Ba(ClO_4)_2$ (anhy.)	26 to 36	2.3 to 3.7	0.82 (0.76-0.88)
NaOH (sticks)	75 to 170	2.3 to 8.9	0.80 (0.78-0.83)
$CaCl_2$ (anhy.)	75 to 240	1.2 to 7.8	0.36 (0.33-0.38)
$Mg(ClO_4)_2 \cdot 3H_2O$	65 to 160	4.0 to 7.2	0.031 (0.028-0.033)
Silica gel	65 to 135	6.5 to 7.7	0.03 (0.02-0.04)
KOH (sticks)	55 to 65	3.2 to 7.2	0.014 (0.010-0.017)
Al_2O_3	65 to 135	6.5 to 7.7	0.005 (0.004-0.009)
$CaSO_4$ (anhy.)	75 to 150	1.2 to 18.5	0.005 (0.004-0.006)
CaO	60 to 90	7.6 to 10.1	0.003 (0.003-0.004)
$Mg(ClO_4)_2$ (anhy.)	95 to 130	6.4 to 13.2	0.002 (0.002-0.003)
BaO	64 to 66	10.6 to 25.0	0.00065 (0.006-0.0008)

Figure 6-25. Comparative efficiency of various drying agents.

Desiccant	Initial composition	Regeneration requirements		Average efficiency[b] (mg/liter)	Relative capacity[c] (liters)
		Drying time (hr)	Temperature (°C)		
Sodium hydroxide[g]	$NaOH\cdot0.03H_2O$	—	—	0.513	178
Anhydrous barium perchlorate	$Ba(ClO_4)_2$	16	127	0.599	28
Calcium oxide	CaO	6	500, 900	0.656	51
Magnesium oxide	MgO	6	800	0.753	22
Potassium hydroxide[g]	$KOH\cdot0.52H_2O$	—	—	0.939	18.4
Mekohbite[g]	68.7% $NaOH$	—	—	1.378	68
Anhydrous magnesium perchlorate[d]	$Mg(ClO_4)_2.0.12H_2O$	48[e]	245[e]	0.0002	1168
Anhydrone[d, f]	$Mg(ClO_4)_2.1.48H_2O$	—	240	0.0015	1157
Barium oxide	96.2% BaO	—	1000	0.0028	244
Activated alumina	Al_2O_3	6 to 8	175,400	0.0029	263
Phosphorus pentoxide[g]	P_2O_5	—	—	0.0035	566
Molecular sieve 5A[f]	Calcium aluminum silicate	—	—	0.0039	215
Indicating anhydrous magnesium perchlorate[d]	88% $Mg(ClO_4)_2$ and 0.86% $KMnO_4$	48[e]	240[e]	0.0044	435
Anhydrous lithium perchlorate[g]	$LiClO_4$	12[e], 12	70[e], 110	0.013	267
Anhydrous calcium chloride[j]	$CaCl_2.0.18H_2O$	16[e]	127[e]	0.067	33
Drierite[f]	$CaSO_4.0.02H_2O$	1 to 2	200 to 225	0.067	232
Silica gel	—	12	118 to 127	0.070	317
Ascarite[f]	91.0% $NaOH$	—	—	0.093	44
Calcium chloride[g]	$CaCl_2.0.28H_2O$	—	200[e]	0.099	57
Anhydrous calcium chloride[g]	$CaCl_2$	16[e]	245[e]	0.137	31
Anhydrocel[f]	$CaSO_4.0.21H_2O$	1 to 2	200 to 225	0.207	683

[a] Nitrogen at an average flow rate of 225 ml/min was passed through a drying train consisting of three Swartz drying tubes (14 mm i.d. by 150 mm deep) maintained at 25 °C.

[b] The average amount of water remaining in the nitrogen after it was dried to equilibrium.

[c] The average maximum volume of nitrogen dried at the specified efficiency for a given volume of desiccant.

[d] Hygroscopic.

[e] Dried in a vacuum.

[f] Trade name.

[g] Deliquescent.

Figure 6-26. Comparative efficiencies and capacities of various solid desiccants in drying a stream of nitrogen.[a]

Silica gel is easy to handle, and it can readily and indefinitely be regenerated at temperatures near 120 °C (4, 10). Attempting to regenerate silica gel above 260 °C will cause loss of the water vapor extractive properties. More often, a series of adsorbents are used for drying a gas stream. A popular series method for water vapor removal is silica gel followed by molecular sieve. The silica gel, which can be regenerated easily, removes a major portion of the water vapor; then the molecular sieve, which is a more efficient drying agent, removes most of the remaining water vapor.

Calcium sulfate also has excellent regenerative capabilities (1-2 hours at 200°C); however, unlike silica gel it will gradually lose its drying properties because of the destruction and reformation of the dehydration elements. Calcium sulfate is also able to operate at a constant efficiency over a wide range of temperatures. Drierite and Anhydrocel are trade names for commercially available calcium sulfate mixtures, and, as with silica gel, these adsorbents are available in indicating and non-indicating forms. Anhydrous magnesium perchlorate has the best drying efficiency of the compounds named, but it has a certain drawback: explosive compounds may be formed if the regeneration step occurs in the presence of organic vapors. For this reason, hydrocarbons must be removed from the gas stream before regeneration (10). Anhydrous magnesium perchlorate is also deliquescent, i.e., it will melt when removing moisture from the air.

Absorption

Absorption is another method of drying a gas stream. Absorption, usually with liquid desiccants, is not as efficient as with solid desiccants, but it has a higher drying capacity because the liquid can be constantly recirculating. This process with liquid desiccants takes place in much the same way as in a scrubbing tower: the gas comes into contact with the liquid and the water vapor is absorbed. Strong acids and bases are good liquid desiccants, but they will emit corrosive vapors.

Condensation

Drying gases by condensation (cooling) is an excellent method for some purposes; all that is required is that the gas be cooled below its dewpoint, thereby removing the water vapor from the gas stream (5). The process is quite simple; the sample gas enters a vessel and is cooled. When the gas has been cooled below the dewpoint, the water vapor condenses on the inner walls of the vessel and is removed from the gas stream, e.g., a solution of dry ice and acetone at a temperature of −78.5°C will remove all but 0.01 mg/liter, and a cooling bath of liquid nitrogen at a temperature of −196°C will remove all but 1×10^{-23}mg of water vapor/liter of air (10). Figure 6-27 lists various cold bath solutions and their temperatures.

Coolant	Temperature °C
Ice and water[a]	0
Ice and NaCl	-21
Carbon tetrachloride slush[a,b]	-22.9
Chlorobenzene slush[a,b]	-45.2
Chloroform slush[a,b]	-63.5
Dry ice and acetone[a]	-78.5
Dry ice and cellosolve[a]	-78.5
Dry ice and isopropanol[a]	-78.5
Ethyl acetate slush[a,b]	-83.6
Toluene slush[b]	-95
Carbon disulfide slush[a,b]	-111.6
Methyl cyclohexane slush[a,b]	-126.3
n-Pentane slush[b]	-130
Liquid air	-147
Isopentane slush[b]	-160.5
Liquid oxygen	-183
Liquid nitrogen	-196

[a] Adequate for secondary temperature standard.

[b] The slushes may be prepared by placing solvent in a Dewar vessel and adding small increments of liquid nitrogen with rapid stirring until the consistency of a thick milkshake is obtained.

Figure 6-27. Summary of cold bath solutions.

Mechanical refrigeration devices especially designed for water removal are commercially available.

Summary

Molecular sieves and activated carbon are used extensively for removal of gaseous contaminants. These solid adsorbents have a porous quality that gives them an extremely high surface area per unit weight, thus increasing their adsorptive capacities.

There are adsorbents and absorbents that will selectively remove one gas from an air stream and leave the others. These include Hopcalite for selectively removing CO from an air stream, manganese dioxide for removing ozone from an air stream, Ascarite for removing CO_2 from an air stream and triethanolamine on firebrick for selectively removing NO_2 from an air or NO stream.

For the removal of water vapor, there are basically three methods used: condensation, absorption and adsorption. Condensation is the most efficient means of drying a gas stream, but may be awkward to use. Absorption, using liquid desiccants, has the greatest capacity for drying a gas stream because the liquid can be recirculated continuously. This method, too, may be awkward for field work. Adsorption of water vapor using solid adsorbents is used extensively because of the ease of handling and storage and the advantage of the regenerative properties.

Sample Problems

Problem 1

A sample gas stream containing sulfur dioxide is to be scrubbed with an adsorbent while the sample collection is performed. The SO_2 concentration is known to be approximately 10 ppm (10 $\mu\ell/\ell$. The adsorbent to be used is activated carbon. The sampling rate is 200 ℓ/min to be maintained for 24 hours. How much activated carbon would be needed to remove all of the SO_2 for the entire length of the sampling period?

Solution

The total amount of sampled air can be calculated 200 ℓ/min × 60 min/hour × 24 hour = 288,000 liters.

The total amount of SO_2 that must be scrubbed from the sample is calculated: 288,000 ℓ of Air × 10 $\mu\ell$ of SO_2/ℓ of Air = 2,880,000 $\mu\ell$ of SO_2 to be removed. For the purposes of this example 1 mℓ = 1cm^3 (this will actually add very little error). 2.88×10^6 $\mu\ell$ $SO_2 \times 10^{-3}$ m$\ell/\mu\ell \times$ 1 cm^3/mℓ = 2880 cm^3 of SO_2 to be removed.

From Figure 6-21, activated carbon will adsorb 380 cm^3 of SO_2 per gram of adsorbent (assuming adsorption takes place at 15 °C).

The total carbon that is necessary can be calculated:

$$\frac{2{,}880 \text{ cm}^3 \text{ SO}_2}{380 \text{ cm}^3 \text{ SO}_2/1 \text{ g Carbon}} = 7.6 \text{ g Carbon}$$

7.6 grams of carbon would be needed to effectively remove the SO_2 from the gas sample. This is an approximate amount.

Problem 2

A sample stream contains approximately 2% (by weight) water vapor, which must be removed. Molecular Sieve Type 4A has been chosen as the drying agent. Sampling is to be performed at 2.5 ℓ/min for 8 hours. How much 4A molecular sieve is needed to dry the air for the length of the sample period? (Assume adsorption takes place at 25 °C).

Solution

The total amount of air sampled:

2.5 ℓ/min × 60 min/hour × 8 hours = 1200 liters.

The density of air at 25 °C and 1 atm (13) is 1.1844 mg/mℓ.

The weight of the air sampled:

= 1200 liters × 1000 mℓ/ℓ/ × 1.1844 mg/mℓ = 1,421,300 mg of air sampled.

The weight of water vapor to be removed:

1,421,300 mg × 0.001 g/mg × 0.02 = 28.43 g.

From Figure 6-24, 4A molecular sieves will remove 24.5 g of H_2O per 100 g of sieve.

The amount of sieve necessary to fully dry the air stream (this is an approximate value):

$$\frac{28.43 \text{ g H}_2\text{O}}{24.5 \text{ g H}_2\text{O}/100 \text{ g sieve}} = 116 \text{ g of Molecular sieve 4A}$$

Summary

Standard test atmospheres are very important as calibration sources for atmospheric monitors. The bag-filling method is best suited for "batch" calibration purposes where only a small amount of calibrated gas is needed at one time. For example, a series of known CO concentrations can be made very quickly with this technique. The cylinder method, permeation tube method, and ozone generators are best used where a constant flow of calibration gas is needed. Some continuous atmospheric monitors and all manual sampling trains require this type of calibration technique because of the finite time required to obtain an adequate sample.

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Chapter 7

Standard Methods for Criteria Pollutants

Introduction

At the present time, there are seven pollutants for which the Environmental Protection Agency has promulgated primary and secondary ambient air quality standards. These pollutants are listed in Figure 7-1(1) together with the averaging time and reference measurement methods. These primary or health related and secondary or welfare related pollutant standards are contained in Title 40 Part 50 of the Code of Federal Regulations (40 CFR 50) and were set forth by the authority granted in Section 109 of the Clean Air Act (1977) (2). The legal methods for monitoring ambient atmospheres for these seven pollutants are contained in the appendices (Appendix A through G) of Part 50. Calibration procedures are also prescribed.

Section 109 of the Clean Air Act as amended in 1977 requires the Environmental Protection Agency to evaluate the criteria for which standards have been promulgated at five-year intervals and to issue any new standards as may be appropriate. The issuance of reference methods designed to monitor these criteria pollutants has a legal basis in Section 301 of the Clean Air Act which states that regulations may be promulgated by the Administrator which are necessary to carry out the provisions of the Act. In order to evaluate and ascertain the status of air quality with regard to the criteria pollutants, uniform analytical methods are used to insure consistency and accuracy in the data generated. Since these methods will be required for extensive monitoring (for state implementation plans, prevention of significant deterioration, etc.) other factors considered are cost, availability, and degree of sophistication.

Reference Method, Equivalent Method, and Measurement Principle

By definition, a **reference method** is a "method of sampling and analyzing the ambient air for an air pollutant that is specified as a reference method in the appendices" of Title 40 Part 50 of the Code of Federal Regulations or a method that has been designated as a reference method in accordance with Part 53 of Title 40b. An **equivalent method** is a method of "sampling and analyzing the ambient air that has been designated as an equivalent method in accordance with Part 53 of 40 CFR." Two types of methods may be considered for equivalent method determination:

1. manual method
2. automated method

A reference method may be either a manual method or an automated as well.

If a manual method is to be considered for equivalent designation, it must demonstrate a consistent relationship to the reference method when both methods are used to measure pollutant concentrations in a real atmosphere. For automated methods, each instrument must meet the performance specifications listed in Figure 7-2(5).

Pollutant	Averaging time	Primary[b,c] standards	Secondary[d] standards	Reference[e] method
Sulfur dioxide	Annual arithmetic mean	80 $\mu g/m^3$ (0.03 ppm)		Pararosaniline method
	24 hr	365 $\mu g/m^3$ (0.14 ppm)		
	3 hr	—	1300 $\mu g/m^3$ (0.5 ppm)	
Suspended particulate matter	Annual geometric mean	75 $\mu g/m^3$	60 $\mu g/m^3$ (f)	High volume sampling method
	24 hr	260 $\mu g/m^3$	150 $\mu g/m^3$	
Carbon monoxide	8 hr	10 mg/m^3 (9 ppm)	Same as primary standard	Nondispersive infrared spectroscopy
	1 hr	40 mg/m^3 (35 ppm)		
Ozone	1 hr	0.12 ppm	Same as primary standard	Gas-phase chemiluminescent method with ethylene
Hydrocarbons (corrected for methane)	3 hr	160 $\mu g/m^3$ (f) (0.24 ppm)	Same as primary standard	Flame ionization detection using gas chromatography
Nitrogen dioxide	Annual arithmetic mean	100 $\mu g/m^3$ (0.05 ppm)	Same as primary standard	Gas-phase chemiluminescence with ozone
Lead	Calendar quarter	1.5 $\mu g/m^3$	Same as primary standard	High volume sampling, atomic absorption analysis

[a] Environmental Protection Agency, *Federal Register* 40 CFR 50 p. 4-6 (July 1, 1979).

[b] National standards other than those based on annual arithmetic means, annual geometric means, or quarterly arithmetic means are not to be exceeded more than once per year.

[c] National Primary Standards: The levels of air quality necessary, with an adequate margin of safety, to protect the public health.

[d] National Secondary Standards: The levels of air quality necessary to protect the public welfare from any known or anticipated adverse effects of a pollutant.

[e] Reference method as described by EPA. An "equivalent method" means any method of sampling and analysis which can be demonstrated to have a "consistent relationship to the reference method."

[f] For use as a guideline in assessing implementation plans.

Figure 7-1. National ambient air quality standards[a].

Performance parameter	Units	Sulfur dioxide	Ozone	Carbon monoxide	Nitrogen dioxide	Definitions and test procedures
1. Range	Parts per million	0–0.5	0–0.5	0–50	0–0.5	Sec.53.23(a).
2. Noise	do	.005	.005	.50	.005	Sec.53.23(b).
3. Lower detectable limit	do	.01	.01	1.0	.01	Sec.53.23(c).
4. Interference equivalent						Sec.53.23(d).
Each interferant	do	±.02	±.02	±1.0	±0.02	
Total interferant	do	.06	.06	1.5	.04	
5. Zero drift, 12 & 24 hr	do	±.02	±.02	±1.0	±.02	Sec.53.23(e).
6. Span drift, 24 hr						Do.
20% of upper range limit	Percent	±20.0	±20.0	±10.0	±20.0	
80% of upper range limit	do	±5.0	±5.0	±2.5	±5.0	
7. Lag time	Minutes	20.	20.	10	20	Do
8. Rise time	do	15	15	5.	15	Do
9. Fall time	do	15	15	5	15	Do
10. Precision						Do
20% of upper range limit	Parts per million	.01	.01	.5	.02	
80% of upper range limit	do	.015	.01	.5	.03	

Figure 7-2. Performance specifications for automated methods. For definitions of the various performance parameters see Reference 5 of this chapter.

The distinction between automated reference and equivalent methods is based upon the measurement principle that an instrument employs. For example, the measurement principle for the automated method for the detection of the oxides of nitrogen is chemiluminescence with ozone. Any instrument, therefore, which meets the performance specification for automated methods *and* uses chemiluminescence with ozone for detection is a reference method. Instruments using other measurement principles would be designated equivalent methods provided they meet the performance specifications. This section is designed to provide a brief overview of the reference methods as they are described in the *Federal Register*, discuss potential problem areas and give some quality assurance considerations from a practical standpoint.

Sulfur Dioxide

The reference method for the measurement of sulfur dioxide in ambient atmospheres is a manual wet-chemical method – the Pararosaniline Method. Sulfur dioxide is bubbled through a solution of potassium tetrachlorosulfitomercurate (TCM) which forms a dichlorosulfitomercurate complex. This complex forms an intensely colored solution upon addition of pararosaniline and formaldehyde. The concentration of sulfur dioxide can be determined spectrophotometrically by measuring the absorbance of the colored solution.

The potential problems associated with interferences are minimized by the procedures listed in Figure 7-3.

Interferent	Corrective procedure
Ozone	time delay
heavy metals	addition of EDTA and Phosphoric Acid
oxides of Nitrogen	addition of Sulfamic Acid

Figure 7-3. Pararosaniline interferences.

Other precautions to be considered relate to the sampling train (Figure 7-4) and sampling conditions. The diameter of the impinger should be checked "such that a No. 79 jewelers drill will pass through but a No. 78 jewelers drill will not(6)." The temperature instability of the dichlorosulfitomercurate complex during sampling also poses potential problems. This can be minimized by using a temperature controlled sampling apparatus (7). Collected samples should be kept at a temperature less than 5 °C. Since this method involves a laboratory analysis of the sample after collection in the field, care should be taken in handling the sample once it has been collected to avoid contamination.

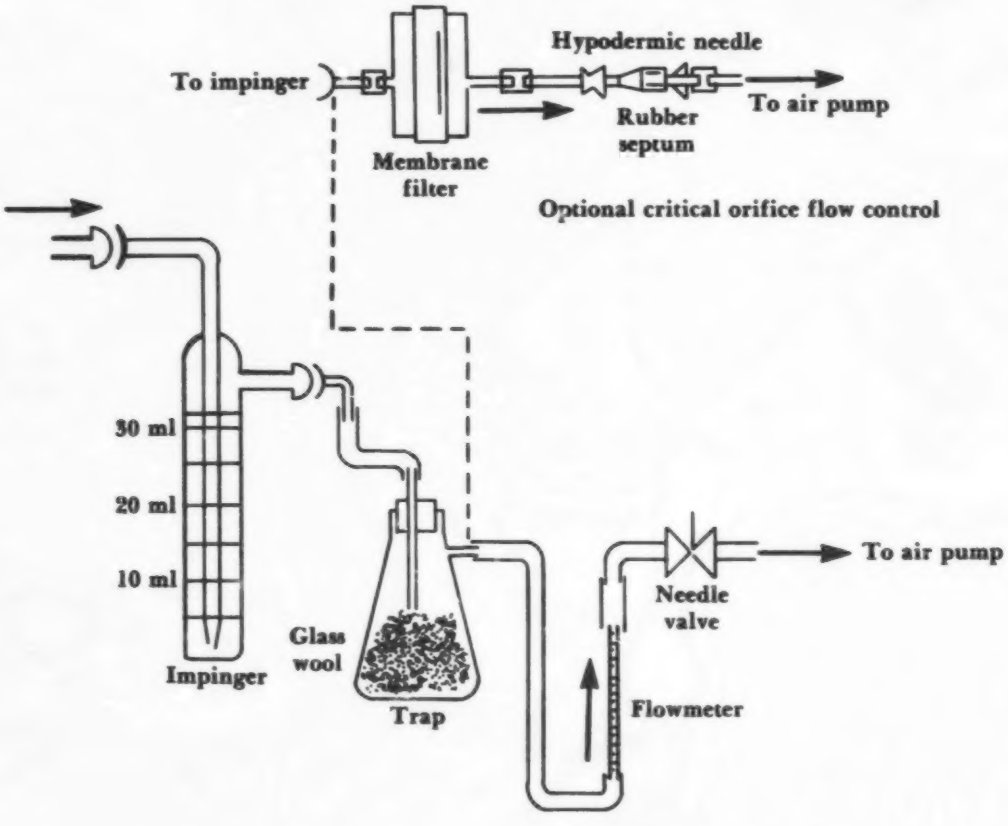
To impinger
Hypodermic needle
To air pump
Rubber septum
Membrane filter
Optional critical orifice flow control
30 ml
20 ml
10 ml
Impinger
Glass wool
Trap
Needle valve
To air pump
Flowmeter

Figure 7-4. Manual SO_2 sampling train for 30 minute to 1 hour sampling.

Nitrogen Dioxide

The reference method for the determination of nitrogen dioxide involves the gas phase chemiluminescence reaction of nitric oxide with ozone (Eq. 7-1). A more complete discussion of chemiluminescence is given in Chapter 8.

(Eq. 7-1) $NO + O_3 \rightarrow NO_2 + h\nu \text{ (light)}$

Nitrogen dioxide is measured indirectly by measuring total oxides of nitrogen ($NO_x = NO_2 + NO$) and electronically subtracting nitric oxide concentration yielding a nitrogen dioxide determination. A measure of the total oxides of nitrogen is obtained by passing the sample across a catalytic converter which reduces nitrogen dioxide to nitric oxide (Eq. 7-2).

(Eq. 7-2) $NO_2 + NO + \text{catalytic converter} \rightarrow NO$

The calibration of the NO and NO_x channels of the instrument is accomplished by diluting a pressurized tank of NO. The calibration of the NO_2 channel is accomplished with a permeation device or the gas phase titration of an NO standard with ozone. The gas phase titration involves the following reaction (Eq. 7-3).

(Eq. 7-3) $NO + O_3 \rightarrow NO_2$

This produces a known amount of nitrogen dioxide which allows one to calibrate the NO_2 channel of the monitor. The other calibration procedure specified in Appendix F. 40 CFR 50 uses a dynamic dilution system in combination with a permeation device to produce a known amount of NO_2. The use of permeation devices and dynamic calibration procedures are discussed in Chapter 6 of this manual.

The problem areas associated with this method are interferents such as peroxyacetyl nitrate and other nitrogen containing compounds (8). In periods of high photochemical activity, corrections for these interferences may be necessary. A recent smog chamber study (9) indicated that the presence of high levels of halocarbons gave a positive interference in a reference method NO_2 analyzer.

The chemical composition of the atmosphere plays an important role in determining the validity of the nitrogen dioxide measurements obtained using a reference method analyzer. For most ambient air measurements, however, interferents such as the ones mentioned previously are minimal. The frequency of calibration and other maintenance (e.g., replacement of charcoal ozone filter, check of converter efficiency, etc.) are important quality assurance considerations.

Carbon Monoxide

The reference method used to measure ambient levels of carbon monoxide is nondispersive infrared spectrometry. A complete discussion of the principle of operation of an NDIR spectrometer is contained in Chapter 8. In brief, a signal is produced as a result of the infrared absorption of carbon monoxide which can be related to the absolute concentration by calibrating the instrument as specified in Appendix C of 40 CFR 50.

The problem areas associated with this method are the broad band absorption of carbon dioxide and water vapor. These two compounds' absorption result in an interference. The technique of a "negative filter" NDIR analyzer (discussed in detail in Chapter 8) corrects for these problems to a limited extent.

Total Suspended Particulate Matter

The High Volume Method is the reference method for the determination of total suspended particulates in ambient air. In this method, air is drawn through a glass fiber filter and the amount of particulate matter is determined gravimetrically. The glass fiber filter is used to collect the particulate matter in a sampler as illustrated in Figure 7-5. A rotameter, attached to the sampler motor near the exhaust port, is calibrated against actual air-flow with an orifice calibration unit (Figure 7-6). This orifice calibration unit is first calibrated against a standard roots-meter®. A detailed description of the calibration procedure is in Chapter 4.

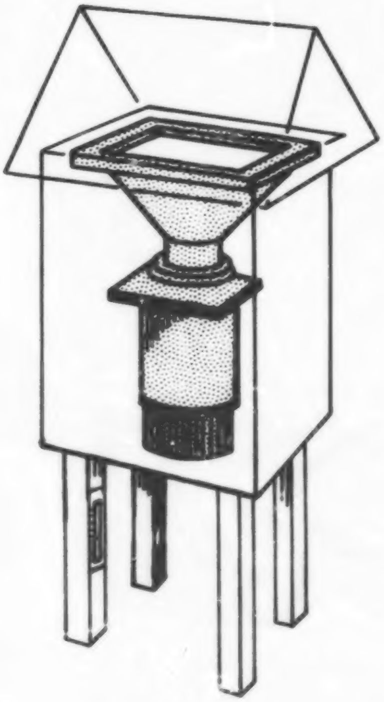

Figure 7-5. Assembled sampler and shelter.

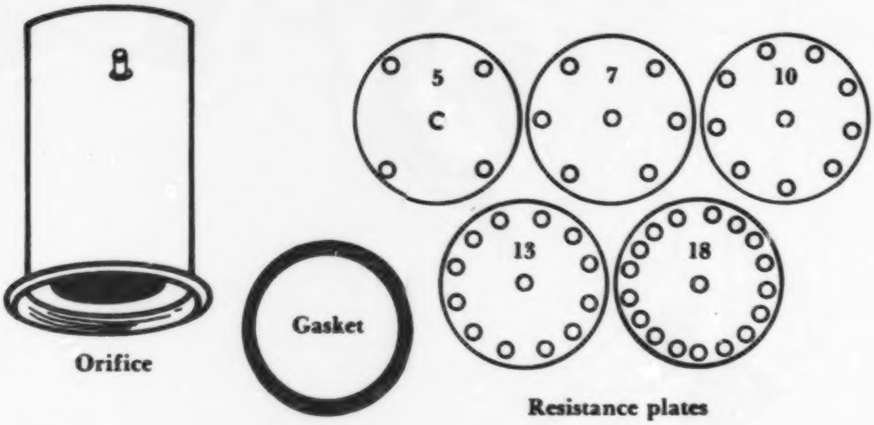

Figure 7-6. Orifice calibration unit.

The problems with this method are the non-uniformity of sampling flow rate, artifact formation of sulfates and nitrates, and the wind direction sensitivity of the apparatus. These problems are discussed more fully in the High Volume section of Chapter 4.

Ozone

The measurement principle for the measurement of ozone is the gas-phase chemiluminescence resulting from the reaction of ozone with ethylene. The unstable nature of ozone requires that ozone be generated *in-situ* in order to calibrate ozone monitors. The NBKI wet-chemical procedure which was previously used to measure ozone concentration from ozone generators demonstrated some "inherent shortcomings" (10). UV photometry was found the most satisfactory for the measurement of ozone concentrations generated *in-situ* and has been designated the calibration procedure. An 18-month phase-in period using a Boric Acid Potassium Iodide procedure began February 8, 1979 (10) to permit air monitoring agencies to acquire and train personnel to operate UV photometers. Figure 7-7 (10) illustrates the BAKI calibration system option and a schematic of the UV photometry calibration system is shown in Figure 7-8.

Nonmethane Hydrocarbons

The reference method for the determination of nonmethane hydrocarbons is gas chromatography with a flame ionization detector (FID). Hydrocarbons are separated from water, carbon dioxide, and methane by a stripper column and a measurement of "total hydrocarbon" is obtained.

Of all the gaseous reference methods, this method is the least reliable. Since different hydrocarbons have different responses to a FID, "total hydrocarbon" measurements are subject to question. The "calibration gas" is simply not specified in the method and, therefore, any hydrocarbon or mixture of hydrocarbons may be used.

Research by some instrument companies has involved converting all hydrocarbons to carbon dioxide or methane and then performing a CO_2 or CH_4 measurement (11). These instruments in principle could operate similar to water "total organic carbon" analyzers.

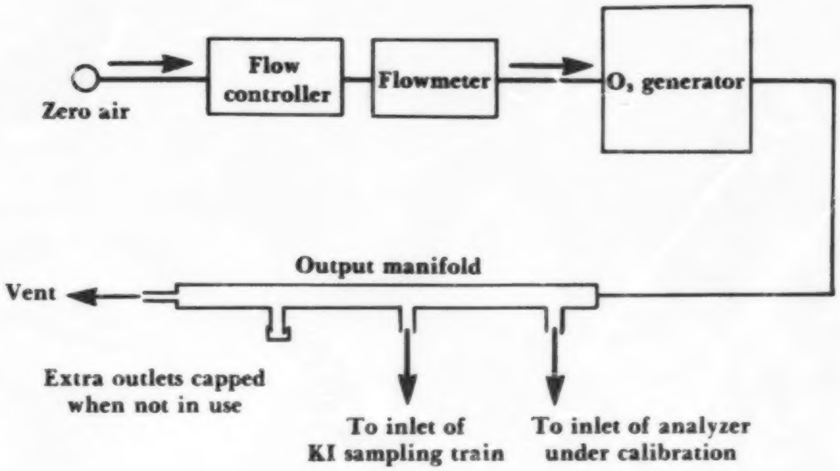
Zero air
Flow controller
Flowmeter
O_3 generator
Output manifold
Vent
Extra outlets capped when not in use
To inlet of KI sampling train
To inlet of analyzer under calibration

Figure 7-7. Schematic diagram of a typical BAKI calibration system.

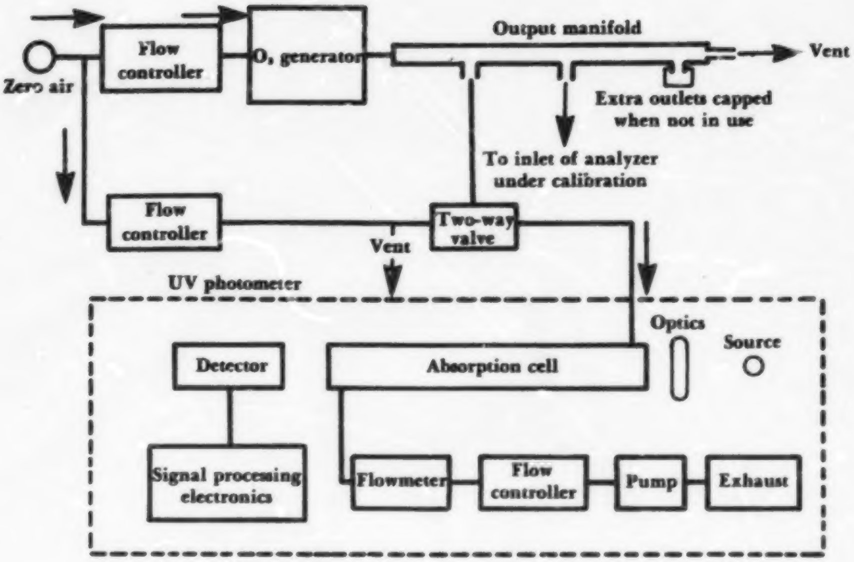
Zero air
Flow controller
O_3 generator
Output manifold
Vent
Extra outlets capped when not in use
To inlet of analyzer under calibration
Flow controller
Two-way valve
Vent
UV photometer
Optics
Source
Detector
Absorption cell
Signal processing electronics
Flowmeter
Flow controller
Pump
Exhaust

Figure 7-8. Schematic diagram of a typical UV photometric calibration system.

Lead

The reference method for lead consists of measuring the lead content of particulate matter collected by the total suspended particulate reference method's high volume sampling procedure. After sample collection, lead is acid extracted from the particulate matter of a ¾" × 8" strip of the high volume filter. Finally, the lead content of the resulting solution is determined by atomic absorption spectrometry (12).

Potential problems exist in both the sampling and analysis portions of the method. In addition to the sampling problems associated with the reference method for total suspended particulates, which were discussed in Chapter 4, lead is non-uniformly distributed across the filter when sampling near heavily traveled roadways. The problem can be alleviated by analyzing a larger portion of the filter. Chemical and light scattering interferences may be encountered during the atomic absorption spectrophotometric analysis. Chemical interferences can be overcome by using the method of standard additions. Light scattering interferences can be corrected by using a dual channel atomic absorption spectrophotometer equipped with a continuum light source, by using a non-absorbing wavelength that is near the lead analytical wavelength, or by using a chelating agent. Furthermore, for accurate particulate lead analyses it is necessary that the variation of lead content from filter to filter within a given batch of blank filters be small (12).

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Chapter 8

Continuous Air Monitoring Instrumentation

Introduction

Instrumental methods are assuming an increasingly prominent role in monitoring gaseous pollutants in air. The advantages of instrumental methods, together with advances in the associated technology, have made older wet-chemical methods largely obsolete. Real-time data output, greater sensitivity in meeting the requirements of specific applications, *in-situ* measurement, and the ability to input directly into computer data systems represent major advantages of instrumental techniques.

The methods that are used for the measurement of oxides of nitrogen exemplify the advantages of an instrumental method. The wet-chemical techniques involve analyzing a grab sample (phenoldisulfonic acid method) for source samples and a 24-hour sample (TGS-ANSA or Sodium Arsenite method) for ambient samples. These techniques, while reliable and relatively inexpensive, require considerable sample handling and lack real-time data output. Moreover, for ambient air monitoring, a short term (less than 24 hours) averaging time requirement will be promulgated by the Environmental Protection Agency. This requirement will reduce the applicability of the wet-chemical methods since they were developed specifically for 24-hour samples. The development of a continuous instrumental method that measures the chemiluminescence produced by the reaction of nitric oxide and ozone has provided a reliable real-time method for the measurement of oxides of nitrogen. This method has been applied to both source and ambient *in-situ* monitoring.

Optical techniques using chemiluminescence and other spectroscopic properties of molecules provide the basis for many continuous air monitoring instruments. These instruments utilize characteristics of a gaseous pollutant that are relatively specific for that molecule. The ultraviolet absorption of ozone and infrared absorption of carbon monoxide are examples of the spectroscopic properties measured in instrumental methods. The ability of a particular pollutant to oxidize halogens is also used in continuous monitors. This section deals with the advantages, disadvantages, principles of operation, and current applications of instruments using physical and chemical properties of air pollutants.

Coulometric Instruments

Principles of Operation

Coulometric analytical techniques use the electrical charge generated by oxidation-reduction reactions occurring in an electrolytic cell to measure gaseous pollutant concentrations. The air sample containing the pollutant flows through the cell and oxidizes (or reduces) part of the solution at one electrode. A balancing reaction occurs at the other electrode causing a small current to flow across the cell. The concentration can be determined by Faraday's Law, which states that one gram-equivalent of a material is oxidized or reduced by one Faraday of electricity. By measuring the current across the cell, the concentration of the sample may be determined since the quantity of electricity (Q, coulombs) is given as the integral of current (i, amperes) over the time interval (t, seconds) (1):

(Eq. 8-1)

$$\int_0^t (i)dt = Q = \frac{zmF}{M}$$

Where:

m = mass in grams of the species consumed or produced during electrolysis

M = gram molecular weight

z = number of Faradays (equivalents) of electricity required per gram mole (i.e., the number of electrons appearing in the equation for the net reaction of interest)

F = proportionality constant: 96,487 coulombs/mole

This type of coulometric technique measures the amount (i.e., coulombs) of electricity directly produced as the result of a reaction of a pollutant at the electrode.

In current instrumentation, however, pollutant concentration is determined indirectly by measuring the current required to maintain a constant halogen concentration. These halogens are typically bromine (Br_2) or iodine (I_2). The sample gas passes through an electrolytic cell and oxidizes the halogen to halide (for example, Br_2 + pollutant → Br^-), thereby reducing the halogen concentration. The current required to maintain the electrochemical balance is directly proportional to the pollutant concentration. Since current and not charge is measured, these analyzers are properly termed **amperometric** analyzers.

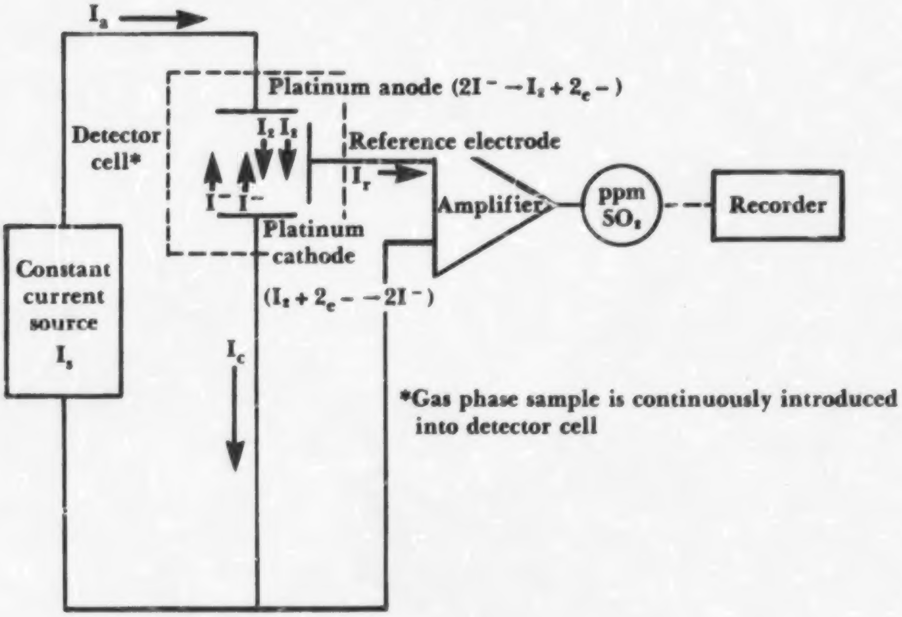
Current Applications

Coulometric or amperometric techniques have been most widely applied to analyzing ambient sulfur dioxide. A constant iodine concentration can be generated by application of a constant current to the electrodes in the detector cell. Upon entering the cell, sulfur dioxide undergoes hydrolysis, and the hydrolysis product reduces the steady state concentration of iodine in the electrolytic cell:

(Eq. 8-2)

$$SO_2 + I_2 + 2H_2O \rightarrow SO_4^{=} + 2I^- + 4H^+$$

Since the iodine concentration has been reduced, the cell loses the capacity to carry the full applied anodic current to the cathode. As a result, current flows through the reference electrode until the electrochemical balance in the cell has been restored. Figure 8-1 illustrates the flow of current and the reactions occuring at each electrode (2).


I_a
Platinum anode ($2I^- \rightarrow I_2 + 2e^-$)
I_2 I_2
Detector cell*
Reference electrode
I_r
I^- I^-
Amplifier
ppm SO_2
Recorder
Platinum cathode
($I_2 + 2e^- \rightarrow 2I^-$)
Constant current source I_s
I_c

*Gas phase sample is continuously introduced into detector cell

Figure 8-1. Coulometric titration of iodine.

Instrumentation also employing this type of coulometric titration measures the reduction of bromine rather than iodine. Typically, bromine concentration is maintained at a constant level by a set of indicator-reference electrodes and the electronic circuits. As sulfur dioxide is introduced into the detector cells, the bromine (Br_2) concentration is reduced by the reaction (8-3):

(Eq. 8-3) $$SO_2 + Br_2 + 2H_2O \rightarrow 2H_2SO_4 + 2Br^- + 2H^+$$

This reaction disturbs the Br_2/Br^- ratio, and this change is sensed by a basic amplifier. The current required to regenerate the bromine (Br_2) through the generator-auxiliary electrodes is proportional to the sulfur dioxide concentration. Figure 8-2 illustrates the four electrodes and circuit employed in this type of instrument (3).

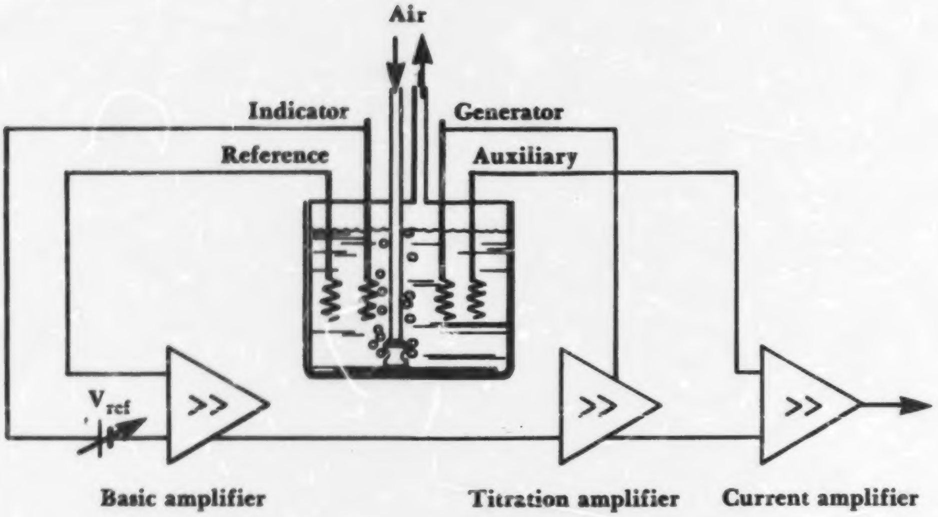


Figure 8-2. Coulometric titration of bromine.

Recently, Lindqvist (4) described a sulfur dioxide monitor based on the anodic oxidation of sulfur dioxide in a galvanic cell. In this type of instrument, sulfur dioxide is oxidized directly by the electrode, and the resulting current can be related to the sulfur dioxide in ambient air. The design of this detector is unique in that current generated by interferences is eliminated by a differential measuring technique. The cell contains two anodes.

One anode is the reference electrode, and the other the measuring electrode. By measuring the potential difference (ΔV) across the cell section when the air flow is equal in both anode sections, the current generated by interferences will be eliminated, and the current will be due solely to the presence of sulfur dioxide. The oxidation of sulfur dioxide at the measuring anode in reaction 8-4 can be related to concentration by Faraday's Law.

(Eq. 8-4)

$$SO_2 + 2H_2O \rightarrow SO_4^{=} + 4H^+ + 2e^-$$

Advantages

As Lindqvist has noted, one of the principle advantages of the coulometric technique for ambient SO_2 monitoring is that these instruments require no compressed gases such as instruments using gas chromatography and flame photometric methods (4). They can, therefore, be used in aircraft and other sites where the use of compressed hydrogen might pose a potential explosion hazard. The major advantage, however, is that coulometric analyzers require minimal maintenance. The halide contained in the cell is regenerated and volatilization of the halogen is not a problem (5). The electrolyte solution that is lost by evaporation can be replaced by condensation from air, or a thermistor (a device for temperature measurement) can be used to automatically maintain the reservoir at a certain level.

Potential Interferents and Disadvantages

The potential interferents in the sulfur dioxide (SO_2) coulometric instruments described here are compounds that are able to oxidize halogens, reduce halogens, or complex with either. Sulfur compounds such as hydrogen sulfide, mercaptans, organic sulfides, and organic disulfides are the most notable interferents. Nitric oxide (NO), ozone (O_3), nitrogen dioxide (NO_2), chlorine (Cl_2), ethane (CH_3CH_3), among others are also interferents but are much less significant than sulfur compounds. Chemical filters to remove these interferents are usually incorporated into coulometric sulfur dioxide analyzers.

Second Derivative Spectroscopic Instruments

Principles of Operation

In direct absorption spectroscopy, pollutant gases absorb energy at a specific wavelength (λ) and the absorption is related to concentration by Beer's Law (Equation 8-5):

(Eq. 8-5)

$$I(\lambda) = I_o(\lambda)e^{-\alpha(\lambda)c\ell}$$

Where:
I_o = *incident intensity at* λ
I = *observed intensity at* λ
c = *concentration of absorbing gas*
ℓ = *path length through the gas*
α = *absorption coefficient of the gas at* λ
e = *natural log function*

Second derivative instruments, on the other hand, relate the slope and curvature characteristics of absorption bands to the concentration of gaseous pollutants. These instruments, rather than produce a second derivative spectrum, produce a signal from which a second derivative voltage output can be extracted. This can be accomplished by using phase lock amplifier circuits. The second derivative voltage output produced by the instrument is directly related to concentration by Equation 8-6 (8).

(Eq. 8-6)

$$\underbrace{S = \left(\frac{d^2I}{d\lambda^2}\right) \Big/ I}_{\textbf{Signal from derivative spectrometer}} = \underbrace{\frac{I}{I_o}\left(\frac{d^2I_o}{d\lambda^2}\right)}_{\textbf{constant, independent of intensity}} \underbrace{- c\ell\left(\frac{d^2\alpha}{d\lambda^2}\right)}_{\textbf{term linear with gas concentration with fixed pathlength}}$$

The method for producing a second derivative signal consists of modulating with time essentially monochromatic light with the amplitude of light approximately equal to the band width being detected. This light is passed through the sample gas and strikes a photomultiplier tube. The $(d^2I/d\lambda^2)/I$ second derivative portion of the signal is extracted by the electronics—"signal analysis"—and can be related to the concentration of the pollutant. Figure 8-3 (7) illustrates the arrangement of the optics employed to produce a second derivative signal.

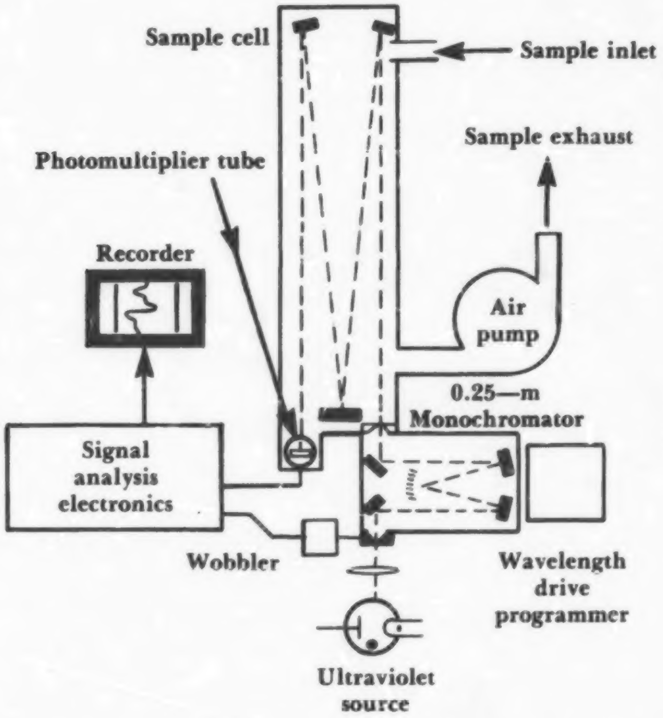

Sample cell
Sample inlet
Sample exhaust
Photomultiplier tube
Recorder
Air pump
0.25—m Monochromator
Signal analysis electronics
Wobbler
Wavelength drive programmer
Ultraviolet source

Figure 8-3. Schematic of optics employed in a second derivative spectrometer.

Since second derivative instruments, like direct absorption spectrometers, do not provide absolute measurements, they must be calibrated with various concentrations of the pollutant being measured.

Current Applications

Second derivative spectrometers are being used to measure both source and ambient pollutants. They have been applied to the measurement of nitrogen dioxide, sulfur dioxide, and ammonia. Another interesting application has been the determination of trace nitrogen dioxide in high purity argon (6).

Advantages

Second derivative spectrometers have the advantage of being highly specific for trace analysis of complex mixtures of atmospheric pollutants (8). Broad band absorption by interferent gases or other light scattered by particulate matter is minimized by these instruments. Also, they have been adapted to *in-situ* stack sampling and unattended ambient monitoring, and the instrumentation employed is relatively simple for single component analysis. Furthermore, no support gases or reactive solutions are required.

Disadvantages

As a practical consideration, the high cost of these instruments in comparison to other instrumental and wet-chemical techniques is the major disadvantage. The mathematical basis for the instrument is complex, and the lack of trained personnel to install, and maintain these instruments are further disadvantages. It should be noted, however, that this technique has only recently been applied to process control, source and ambient monitoring. Its utility, therefore, remains to be determined.

Flame Photometric Instruments

Principles of Operation

Instrumentation employing flame photometric detection measures the emission intensity of a selected wavelength while the pollutant is introduced into a hydrogen-rich flame. Figure 8-4 illustrates the principal components of a flame photometric detector (FPD).

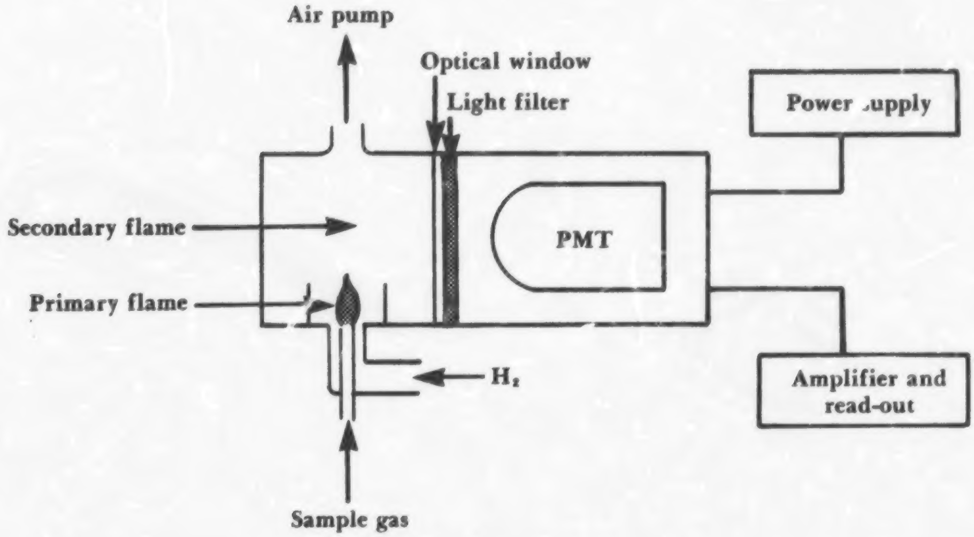


Figure 8-4. Flame photometric detector.

The sample gas containing sulfur pollutants is introduced into the hydrogen-rich flame producing a S_2 species that reacts with the available hydrogen and hydroxyl radicals to produce a high energy species S_2^*. In an excellent review by Farwell et al. (9), the principal reactions involved in the formation of the high energy S_2^* from the sulfur-containing pollutant are discussed. They may be briefly summarized in reactions 8-7 through 8-14.

(Eq. 8-7) $\textit{Sulfur compound} \xrightarrow{heat} \textit{S atoms or indirectly by}$

(Eq. 8-8) $\textit{Sulfur compound} \xrightarrow{heat} H_2S$

(Eq. 8-9) $H_2S + \bullet H \rightarrow HS + H_2$

(Eq. 8-10) $HS \cdot \bullet H \rightarrow S + H_2$

In the cool outer cone of the flame there results in the formation by excited S_2^* molecules by the following set of reactions:

(Eq. 8-11) $\bullet H + \bullet H + S_2 \rightarrow H_2 + S_2^*$

where the recombination of atomic hydrogen furnishes the excitation energy for $S_2 \rightarrow S_2^*$ or by the reaction

(Eq. 8-12) $\bullet H + \bullet OH + S_2 \rightarrow S_2^* + H_2O$

where the formation of H_2O supplied the excitation energy for $S_2 \rightarrow S_2^*$.

The mechanism for the production of strong luminescent emission with the concurrent conversion of the high energy S_2^* to the lower energy state S_2 may be summarized:

(Eq. 8-13) $S_2 + \bullet H + \bullet H \rightarrow S_2^* + H_2$

$$S_2^* \rightarrow S_2 + h\nu$$

or $S + S + M \rightarrow S_2^* + M$ *(where M is a third body)*

(Eq. 8-14) $S^* \rightarrow S_2 + h\nu$

The observed luminescent emission ($h\nu$) is related to the concentration of the sulfur pollutant by Equation 8-15.

(Eq. 8-15) $I_{S_2} = I_o[S]^n$

Where

I_{S_2} = *observed intensity of the molecular emission due to the* S_2 *species*

$[S]$ = *concentration of sulfur atoms*

I_o = *constant under given experimental conditions*

n = *constant (usually assumed to be 2) under given experimental conditions*

It should be noted that the concentration of sulfur pollutant is not linearly proportional to the observed intensity. Most instruments, however, use linearizing electronic circuitry to yield a linear voltage output. Moreover, instruments using FPD must be calibrated with various concentrations of the particular pollutant gas since this measurement is not absolute and different sulfur gases have different responses.

Current Applications

The flame photometric detector is most frequently used in the detection of ambient sulfur dioxide. This instrumentation uses a scrubber to remove potential interferents (usually sulfur compounds other than SO_2) and the signal is converted to a linear ppm SO_2 output. The flame photometric detector in combination with gas chromotography has been used to detect mixtures of sulfur-containing pollutants (SO_2, H_2S, CH_3SH, and others). Stevens, et al. (10), for example, described a gas chromatographic system using flame photometric detection to separate and quantitate various sulfur pollutants.

Potential Interferents

Instrumentation designed to monitor for a specific sulfur compound, such as SO_2, must contain scrubbers that remove all other sulfur-containing compounds. This is a consequence of the fact that the flame photometric detector does not discriminate between different sulfur-containing compounds. Moreover, as Farwell notes (9), the presence of other organic compounds in the sample gas (as well as variable carbon dioxide) may result in a change in the response of the FPD. This change in response may be attributed to "the inactivation of the excited S_2^* species by their combination or collision with organic compounds and/or the organic degradation products." Ambient relative humidity may represent another potential interferent.

Advantages

The principal advantages of FPD analyzers are low maintenance, high sensitivity, fast response, and selectivity for sulfur compounds. There are no solutions, and the only reagents are hydrogen and air for the flame. These analyzers have the potential for unattended operation. They are particularly useful at most ambient air monitoring sites since interference from non-sulfur species is essentially nonexistent (10).

Fluorescence Instruments

Fluorescence emission can be differentiated from other types of luminescence by the type of excitation energy. Chemiluminescence, for example, uses a chemical reaction, x-ray fluorescence uses x-rays, and fluorescence uses ultraviolet-visible light. Fluorescence can be distinguished from phosphorescence mechanistically and empirically by observing the lifetime of the excited states (~ 10^{-8} second for fluorescence; several seconds for phosphorescence). The energy level diagram in Figure 8-5 illustrates the mechanism involved in fluorescence emission (11).

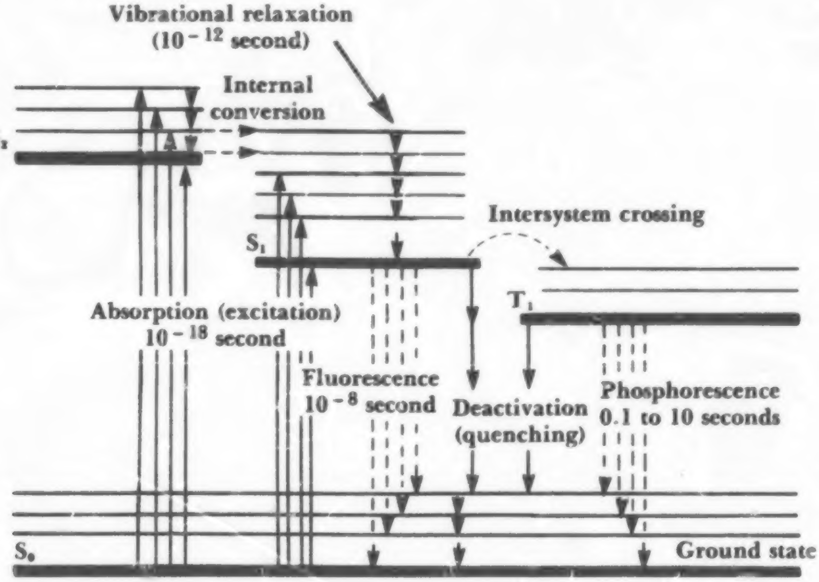

Vibrational relaxation
(10^{-12} second)
Internal conversion
S_2
Intersystem crossing
S_1
T_1
Absorption (excitation)
10^{-18} second
Fluorescence
10^{-8} second
Deactivation
(quenching)
Phosphorescence
0.1 to 10 seconds
S_0
Ground state

Figure 8-5. Energy levels in fluorescence emission.

In fluorescence, the molecule is in a high vibrational state after an electronic transition (e.g., $S_o \rightarrow S_2$). Upon loss of some energy by vibrational relaxation the molecule reverts to the lower energy state by emission of light (e.g., $S_1 \rightarrow S_o$). This radiation is termed fluorescence.

Current Applications

The principle application of fluorescence spectroscopy is for the measurement of ambient and source sulfur dioxide. Okabe et al. (12) first applied this mode of detection to the measurement of sulfur dioxide in 1973. Since that time, commercial monitors have been developed, and these instruments have been designated by the Environmental Protection Agency as equivalent methods for monitoring ambient SO_2. One method, termed "pulsed fluorescence," uses a short pulsed, high-intensity ultraviolet light source in the 2100 Å region to excite the SO_2 molecules. The fluorescence emission that follows is detected by a photomultiplier tube and processed electronically to yield direct ppm SO_2 measurement. These instruments must be calibrated with different concentrations of standard SO_2, since, like other luminescence methods, the method is not absolute.

Advantages

These instruments use no consumable gases, as does the FPD, and the inherent stability enables the instrument to operate for long unattended periods. The instruments are linear over a wide range (0.5-5000 ppm), responsive, and insensitive to temperature and flow variations.

Potential Interferents and Disadvantages

The interferents in "UV fluorescence" instruments are related primarily to the quenching effects of O_2, N_2, CO_2, and water vapor. For ambient monitoring, the level of O_2, N_2, and, for the most part CO_2 and water vapor, are constant, and thus the quenching effect is fairly constant. In flue gases, however, the level of CO_2, water vapor, and O_2 vary considerably. Consequently, the SO_2 values may be spurious. Jahnke et al. (13) have obtained approximate values for the quenching coefficients of these gases providing corrections for different concentrations of CO_2, N_2, and O_2. Hydrocarbons may also interfere but all "equivalent" analyzers now come equipped with a hydrocarbon scrubber or "cutter" to eliminate this potential problem.

Chemiluminescence Instruments

Principles of Operation

Chemiluminescence instruments in air pollution monitoring measure the emission of light produced by the reaction of a gaseous pollutant and a reagent gas. The process involved in homogeneous gas-phase chemiluminescence is summarized in Reactions 8-16 and 8-17.

(R8-16) $$A + B \rightarrow C^* + D$$

(R8-17) $$C^* \rightarrow C + h\nu$$

The reaction of pollutant *A* with excess reagent gas *B* produces a chemi-excited species C^*, which reverts to a lower energy state by emission of light ($h\nu$). The light thus produced passes through an optical filter to isolate a given spectral region and strikes a photomultiplier tube (PMT). The PMT signal is amplified and is directly proportional to the concentration of pollutant (14).

Instrumentation employing this type of chemiluminescence is compound or pollutant specific and should be distinguished from the flame chemiluminescence detector (flame photometric detector) described previously, which is element specific. The flame photometric detectors are used almost exclusively for the measurement of sulfur compounds. The chemiluminescence instruments discussed here use a reagent gas rather than a hydrogen-rich flame to produce a chemi-excited species.

Figure 8-6 illustrates the basic components and gas flow of a compound-specific chemiluminescence detector. Sample gas containing the pollutant enters the reaction chamber and reacts with the reagent gas.

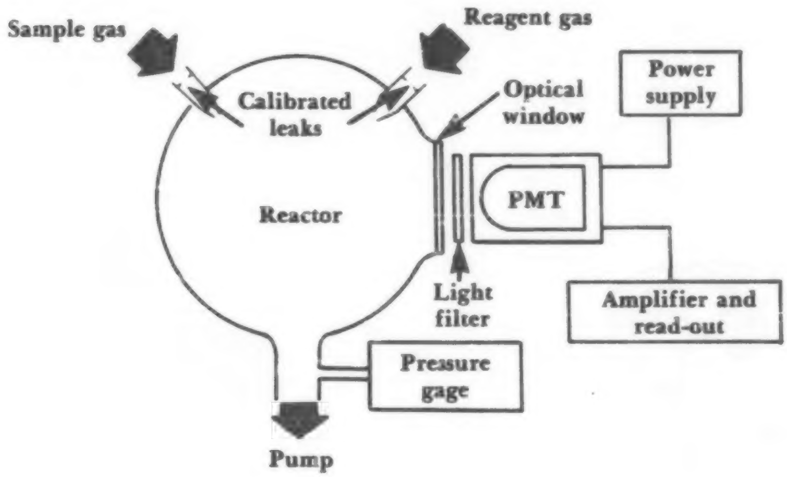

Sample gas
Reagent gas
Calibrated leaks
Optical window
Power supply
Reactor
PMT
Light filter
Amplifier and read-out
Pressure gage
Pump

Figure 8-6. Compound specific chemiluminescence detector.

The intensity of the light produced is related to the concentration of pollutant and reagent gas (Equation 8-16).

(Eq. 8-16) $$I = k[A][B]$$

Where:

I = *intensity of light emitted*
k = *rate coefficient (a constant)*
$[A]$ = *concentration of pollutant*
$[B]$ = *concentration of reagent gas*

Since the reagent gas is usually present in large excess, the concentration is assumed to be constant and Equation 8-17 can be used to relate the intensity to the concentration of pollutant.

(Eq. 8-17) $$I = c[A]$$

Where:

I = *intensity of light emitted*
c = *constant under given experimental conditions*
$[A]$ = *concentration of pollutant*

Current Applications

Chemiluminescence techniques are routinely used for the measurement of ozone and oxides of nitrogen. The chemiluminescence resulting from an ethylene/ozone reaction was first reported by Nederbragt et al. (15) in 1965 and forms the basis for present ozone monitors using homegenous gas-phase chemiluminescence. This reaction produces a continuum at 435 nm presumably due to an excited aldehyde linkage (16). After extensive field testing and evaluation of prototype instruments, ozone/ethylene chemiluminescence was designated as the reference principle for ozone detection by the Environmental Protection Agency (17).

The reaction of ozone (O_3) with nitric oxide (NO) produces an emission spectrum that is shown in Figure 8-7 (15).

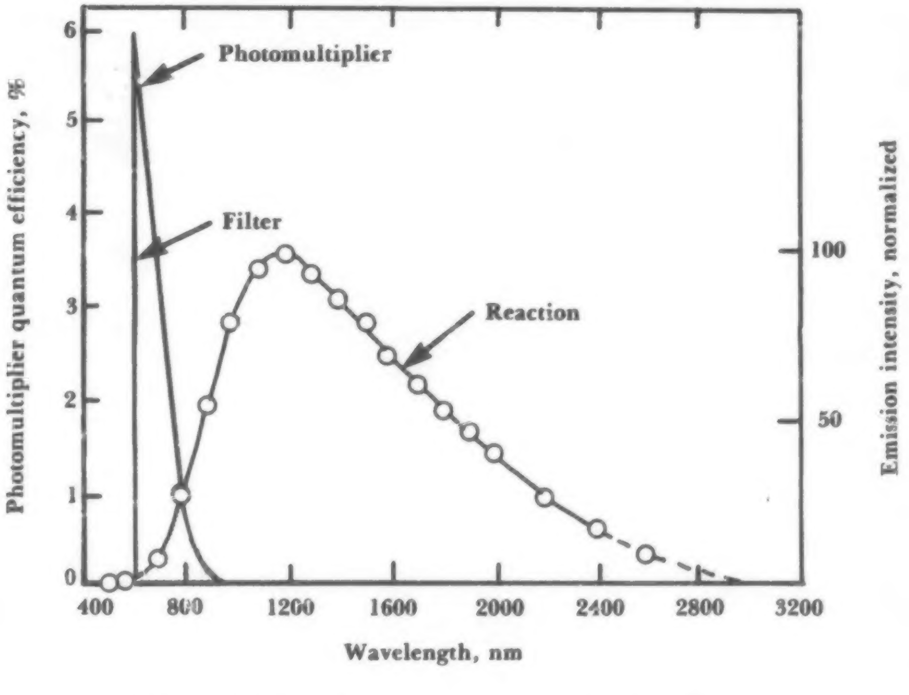


Figure 8-7. Emission spectrum of ozone/nitric oxide.

This spectrum results from the chemiluminescence of ozone and nitric oxide shown in Reactions 8-18 and 8-19.

(Eq. 8-18) $NO + O_3 \rightarrow NO_2^* + O_2$

(Eq. 8-19) $NO_2^* \rightarrow NO_2 + h\nu$

Nitric oxide is measured directly. Nitrogen dioxide measurements can be made by catalytic conversion of nitrogen dioxide to nitric oxide with carbon-based and other metal converters resulting in a total oxide of nitrogen concentration ($NO_x = NO + NO_2$). The difference between total oxides of nitrogen ($NO_2 + NO$) and nitric oxide is a measure of nitrogen dioxide concentration.

Potential Interferents

For a positive interference species must react with the reagent to yield chemiluminescence in the spectral region of the pollutant emission. In nitrogen oxide detectors a filter that absorbs emissions below 600 nm is placed between the reaction chamber and photocathode. This eliminates emissions from the reaction of ozone with olefins that could produce a positive interference. Ambient instruments also respond to other nitrogen pollutants such as peroxyacetyl nitrate, ammonia, and other organic nitrates (18). These nitrogen compounds are converted to NO in the converter. Quenching effects are a source of negative interference. In ambient air, molecular nitrogen and oxygen are the predominate quenching agents; but, since these agents do not vary significantly in concentration the quenching effect is generally constant. In source measurements, carbon dioxide and water vapor are additional quenching agents posing a potential negative interference.

Advantages

The advantages of gas-phase chemiluminescence are that emissions are relatively specific for the pollutant being monitored. Gas-phase reactions in instruments using continuous flow are insensitive to changes in surface properties in the reaction chamber (19). Furthermore, a linear response in the range of 4 ppb to 100 ppm can be obtained.

Ultraviolet Photometric Instruments

Principle of Operation

The visible and ultraviolet absorption of molecules are associated with electronic energy level transitions. For example, $\pi \rightarrow \pi^*$ or $\sigma \rightarrow \sigma^*$ transitions could result in ultraviolet absorption. Instruments making use of the ultraviolet absorption of pollutants measure the absorption at a specific wavelength that can be related to the concentration of the pollutant by Beer's Law (Equation 8-5).

Current Applications

The ultraviolet absorption of ozone is shown in Figure 8-8. This characteristic of ozone will be used to calibrate ozone monitors using chemiluminescent detection by the Environmental Protection Agency after evaluation of UV photometry, a wet

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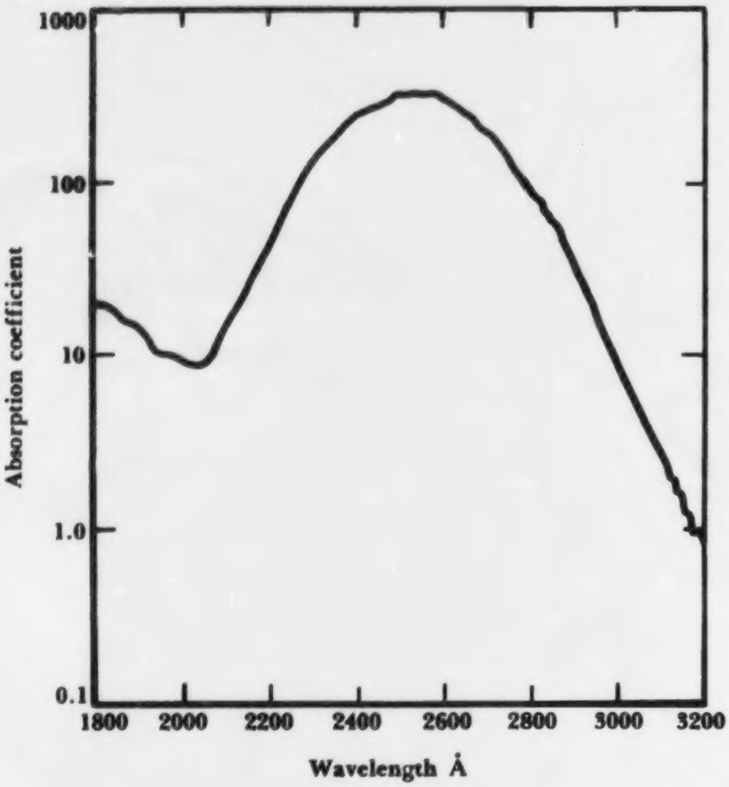


Figure 8-8. Ultraviolet absorption of ozone.

chemical method, and gas-phase titration. The procedure using a UV calibration photometer was shown to "have the best performance—low variability, high accuracy, and minimum operator involvement (20)." Figure 8-9 shows the gas flow and components of an instrument using UV photometry for the detection of ozone (21). The calibration of ambient ozone instruments (chemiluminescence), continuous monitors for source NO_x, SO_2, H_2S, and other gases, and the use of a UV photometer as an analyzer itself are but a few of its current uses.

Advantages

The UV photometry method for calibration of ozone monitors eliminated a wet chemical method—"the NBKI procedure," which had demonstrated "some inherent short-comings (20)." In source applications, instruments measure the difference in absorption of radiation (in the UV-visible region) by the stack gas at two different wavelengths. This provides continuous measurement of gaseous pollutants (NO_x, SO_2, etc.) in stacks. These instruments have numerous advantages over wet-chemical techniques, which require considerable sample handling and lack continuous data output.

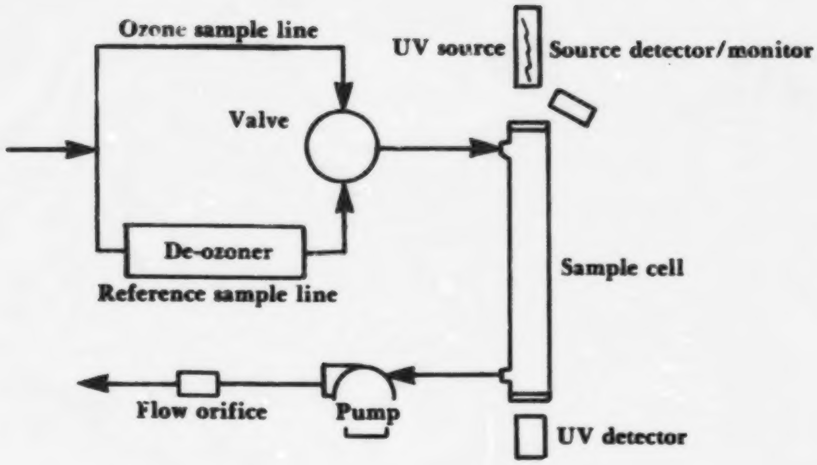


Figure 8-9. Flow and components of ozone detector using UV photometry.

NDIR Instruments

Principle of Operation

Nondispersive infrared (NDIR) analyzers have been developed to monitor SO_2, NO_x, CO, CO_2, and other gases that absorb in the infrared, including hydrocarbons. They are termed nondispersive analyzers because they use no prism or grating to disperse the infrared radiation. A narrow band filter that absorbs all frequencies except the one of interest is used. Figure 8-10 illustrates the essential components and gas flow of a typical NDIR instrument.

Light passes through the sample and reference cell and then through a narrow bandpass filter, which limits the wavelengths of light entering the detector cells to the area of the electromagnetic spectrum at which the pollutant molecule strongly absorbs.

The reference cell is filled with a non-absorbing inert gas such as nitrogen or argon. If no pollutant gas is present in the sample, the amount of radiation reaching the reference half and the sample half of the detector will be equal; therefore, the temperature (and resulting pressure) of both halves of the detector will be equal. Thus, with no pollutant in the sample side, the diaphragm shown in Figure 8-11 is in a null (a zero distention) position.

As pollutant gas enters the sample cell, the energy reaching the sample half of the detector will be less, due to the absorption of energy by the pollutant. This produces a distention of the diaphragm because the temperature (and resulting pressure) is lowered on the sample side of the detector cell. (e.g., the pressure is directly related to the temperature of a gas at constant volume). The distention of the diaphragm produces a capacitance change in the detector that is converted to a voltage output by the instrument. The optical chopper simply creates an alternating current (AC) signal that can be easily amplified.

This technique, while seemingly specific for CO, suffers from interferences due to the broad band absorption of carbon dioxide, water vapor, and hydrocarbons.

Figure 8-11 shows the absorption of carbon monoxide and the broad band interferences.

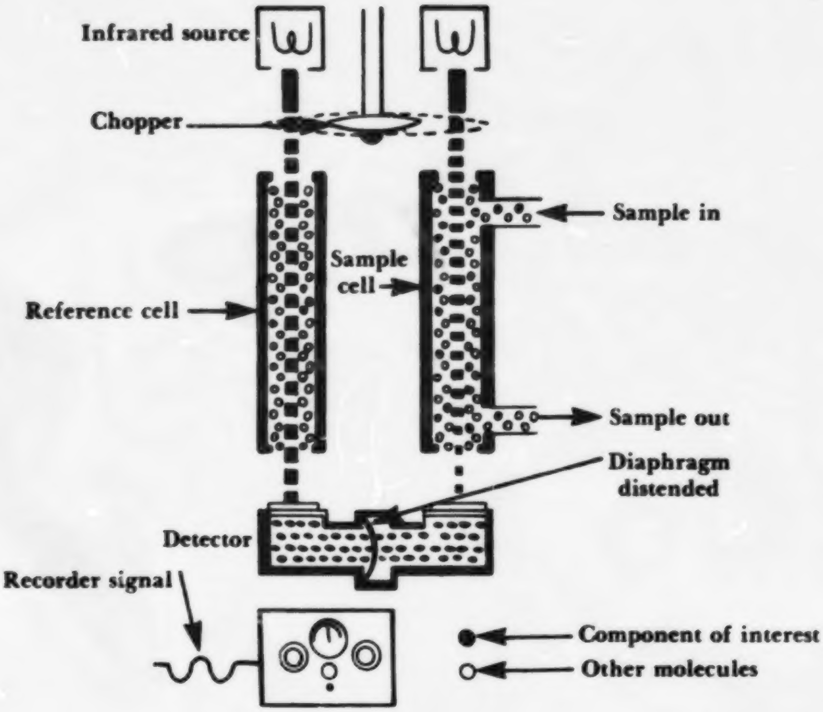

Infrared source
Chopper
Sample in
Sample cell
Reference cell
Sample out
Diaphragm distended
Detector
Recorder signal
Component of interest
Other molecules

Figure 8-10. Components and gas flow of a NDIR instrument.

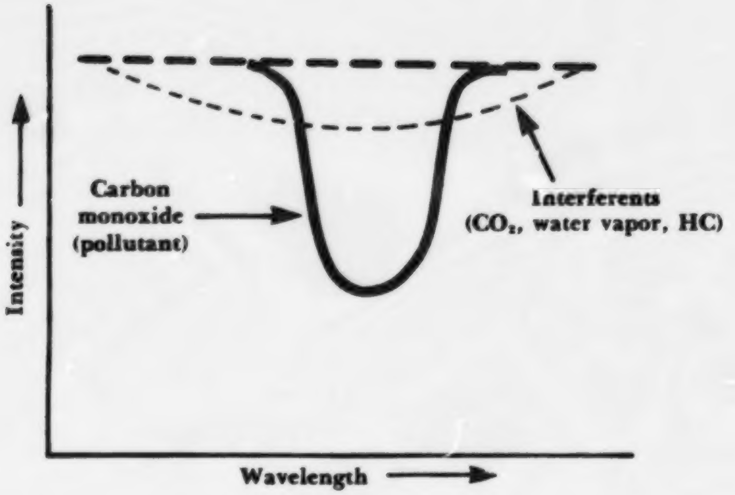


Figure 8-11. Overlap of carbon monoxide and broad band absorption curves.

If broad band interferences were present, the NDIR depicted in Figure 8-11 would yield a higher concentration than was actually present.

An NDIR instrument has been designed that minimizes these broad band interferences. In this type of instrument, two detector cells are placed in series as shown in Figure 8-12.

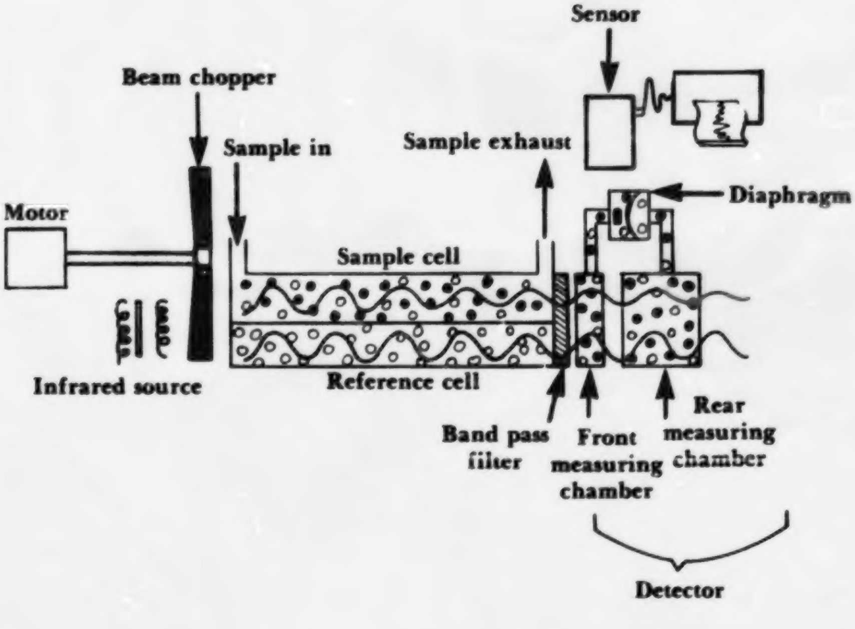
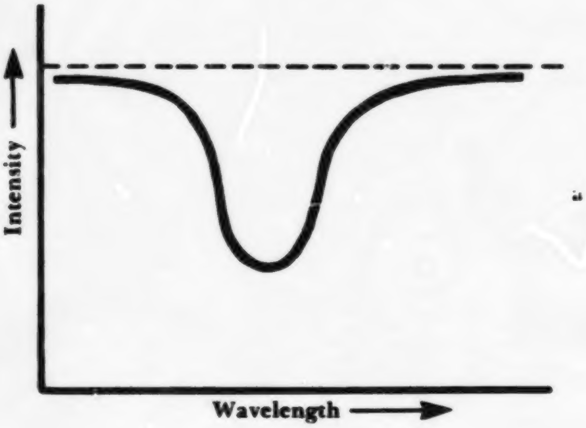
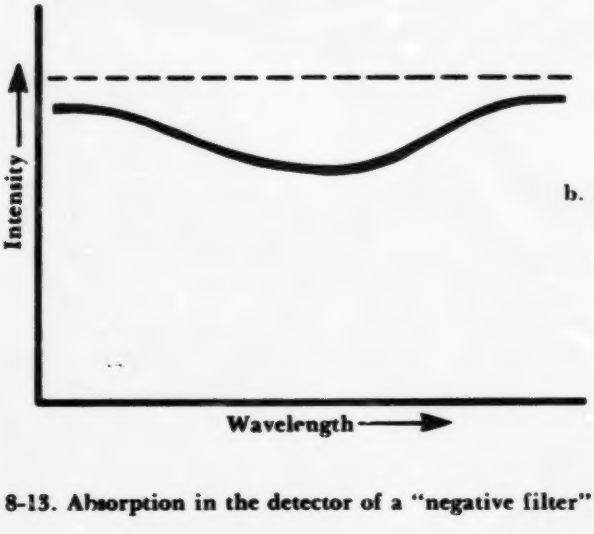

Sensor
Beam chopper
Sample in
Sample exhaust
Diaphragm
Motor
Sample cell
Infrared source
Reference cell
Band pass filter
Front measuring chamber
Rear measuring chamber
Detector

Figure 8-12. "Negative filter" analyzer.

As light enters the sample cell, the gas absorbs energy in the CO spectral region. The carbon monoxide in the front detector cell absorbs the reduced energy from the sample cell, largely from the center frequencies of the CO band (see Figure 8-13a). The rear measuring chamber absorbs the remaining energy (see Figure 8-13b). The longer cell path of the rear measuring chamber allows for more absorption in the rear chamber. The resulting distention in the diaphragm, then, is a ratio of the CO absorption in the front and rear measuring chambers. If the interferences are largely linear across the CO absorption band, this ratio will accurately reflect the CO concentration; that is, the absorbances in the front and rear chambers will increase by the same amount due to interferences, but the ratio will be constant regardless of the amount of positive interference. This technique differs significantly from the NDIR discussed previously and is termed "negative filtering (22)."



a. Front measuring chamber absorbs center frequencies



b. Rear measuring chamber absorbs remaining energy

Figure 8-13. Absorption in the detector of a "negative filter" NDIR analyzer.

Current Applications and Advantages

NDIR analyzers in ambient monitoring are used principally for the measurement of carbon monoxide. This technique has been designated as the reference method for the continuous measurement of carbon monoxide in air by the Environmental Protection Agency. This technique is a relatively inexpensive, reliable method that does not require highly trained personnel for its operation.

Potential Interferents and Disadvantages

Since NDIR spectroscopy is most frequently used in the measurement of carbon monoxide, the two most prominent interferents are carbon dioxide and water vapor. "Negative filter" (22) analyzers discussed previously or more recent analyzers using a palladium catalyst and a flowing reference cell all minimize spectral interferences from CO_2 and water vapor (23). The normal hydrocarbon levels in the atmosphere are too small to cause possible interference in NDIR analyzers.

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Chapter 9

Design of Surveillance Networks

Elements of Surveillance Networks

All ambient air surveillance networks are composed of several major elements that can be divided into two subsystems: a sensor subsystem and a data subsystem. The data subsystem can be further divided into a data recording and transmission system, and a data processing system. This chapter will describe the elements of each subsystem, along with the basic considerations necessary for overall design. It should be remembered throughout this process that designing an ambient air surveillance network is a complex process requiring some experience. There are no easy procedures to follow that will eliminate all potential problems. This chapter will introduce you to a basic approach and will provide you with sufficient information to design basic air monitoring networks.

Defining Network Uses and Objectives

Before beginning considerations for system components for your surveillance network, the ultimate uses of the data must first be identified. The design of an effective network must establish these uses and employ them throughout the design process. For example, several of the major uses for sulfur dioxide (SO_2) data are:

1. Judging attainment of SO_2 NAAQS;
2. Evaluating progress in achieving/maintaining the NAAQS or State/local standards;
3. Developing or revising State Implementation Plans (SIPs) to attain/maintain NAAQS; evaluating control strategies;
4. Reviewing new sources;
5. Establishing baseline air quality levels for preventing significant deterioration (PSD) and for air quality maintenance planning (AQMP);
6. Developing or revising national SO_2 control policies, e.g., new source performance standards (NSPS), tall stacks, supplementary control systems (SCS);
7. Providing data for model development and validation;
8. Providing data to implement the provisions of the Energy Supply and Environmental Coordination Act (ESECA) of 1974;
9. Supporting enforcement actions;
10. Documenting episodes and initiating episode controls;
11. Documenting population exposure and health research;
12. Providing information to:
    a. public—air pollution indices; and
    b. city/regional planners, air quality policy/decision makers—for activities related to programs such as air quality maintenance planning (AQMP), prevention of significant deterioration (PSD), and the preparation of environmental impact statements. (1)

These uses are broad and program oriented and, therefore, serve to delineate the direction of the whole program. The second step in the design process is to generate a list of specific objectives from the above design criteria. To continue the example of SO_2, some of the specific objectives and the associated data uses are as follows (*data use* numbers refer to above list of SO_2 data uses).

1. Determination of peak concentrations in urban areas
   - major data uses: 1, 2, and 3.
   - other data uses: 8, 9, and 12.
2. Determination of the impact of individual point sources in multi-source urban settings
   - major data uses: 3, 4, 6, 8, and 9.
   - other data uses: 12.
3. Determination of the impact of isolated point sources
   - major data uses: 3, 4, 6, 8, and 9.
   - other data uses: 5 and 12.
4. Assessment of interregional SO_2 transport
   - major data uses: 2, 3, 5, and 12.
5. Determination of base concentrations in areas of projected growth
   - major data uses: 5 and 12.
6. Initiation of emergency episode abatement actions
   - major data uses: 10 and 12.
7. Determination of population exposure
   - major data uses: 11 and 12.
8. Assessment of background concentrations in rural areas
   - major data uses: 5 and 12.
   - other data uses: 2 and 3. (2)

Having identified specific objectives, there are some additional general considerations that must be discussed before beginning the actual design of the three subsystems. It should be remembered, however, that these objectives should be the basis for the total design of the surveillance network. They should be prioritized on the basis of several points, including legal requirements, topography, population data, source characteristics, administrative and political concerns, and of course, cost. Some of these topics will be covered in the section following on specific siting procedures. By organizing these objectives by priorities, it should be possible to minimize expense while still meeting the identified needs.

Sensor Subsystem

Having established the why of our monitoring network, we can now begin to choose a sensor system. The first step in choosing an appropriate sensor is to identify what is to be monitored. If we are monitoring for more than one pollutant, it may be necessary to have more than one type of shelter, probe, and monitoring location. For example, measurements made in a street canyon may be valid for determining maximum CO concentrations, but probably are not valid for regional SO_2 measurements. This problem centers around the spatial scale of representativeness of a station.

It is important to be aware of the distinction between the spatial scale *desired* to be represented by a measurement, and the spatial scale ***actually*** represented by that measurement. The spatial scales and the corresponding dimensions characterizing each are:

- **Microscale**. Ambient air volumes with dimensions ranging from meters up to about 100 meters are associated with this scale.
- **Middle Scale**. This scale represents dimensions of the order from about 100 meters to 0.5 kilometers and characterizes areas up to several city blocks in size.
- **Neighborhood Scale**. Neighborhood scale measurements would characterize conditions over areas with dimensions in the 0.5 to 4.0 kilometer range.
- **Urban Scale**. Urban scale measurements would be made to represent conditions over areas with dimensions on the order of 4 to 50 kilometers.
- **Regional Scale**. Conditions over areas with dimensions of as much as hundreds of kilometers would be represented by regional scale measurements. These measurements would be applicable mainly to large homogeneous areas, particularly sparsely populated areas.
- **National and Global Scales**. These measurement scales represent concentrations characterizing the nation and the globe as a whole (3).

These dimensions are approximate but provide useful divisions for defining the final site. Within each scale, there may be more than one site required to define the area: for pollutants that have large, individual sources; for areas with steep concentration gradients (concentrations changing rapidly over relatively short distances); for reactive pollutants. The concentration gradients would be determined from previous sampling or dispersion modeling.

The choice of "what" will be monitored should be based on the needs, uses, and objectives that we defined. At this stage, we should prioritize these needs based on the individual considerations of each case. Each case will represent a unique situation. Some common considerations include:

- Pollutants with legal standards;
- Available resources, material, and personnel;
- Political factors;
- Problem pollutants—expected hazards.

The importance given each of these factors will vary with each case.

Monitoring Methods

The completion of this task leads to the next step in designing the sensor subsystem—how are we going to monitor? If a criteria pollutant is being monitored, one of the EPA Federal reference methods should be considered. These are included in the appendix of this manual. Also available from EPA* is the "List of Designated Reference and Equivalent Methods," which provides a current listing of all the methods for measuring ambient concentrations of specified air pollutants

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*U.S. Environmental Protection Agency
Office of Research and Development
Environmental Monitoring and Support Laboratory
Research Triangle Park, NC 27711

that have been designated "reference or equivalent" methods in accordance with 40 CFR 53. There are cases where you will be required to use a reference or equivalent method such as when monitoring for State Implementation Plans (SIPs) or most monitoring required under the Prevention of Significant Deterioration (PSD) regulations (40 CFR§51.24). If use of the EPA Federal reference or equivalent methods is not required, it is important to ascertain if the method of sampling is specified by a law or statute. If the data is to be used in legal proceedings, this fact may be of considerable importance. Other sources of analytical methods exist including the NIOSH Manual of Analytical Methods and the Annual ASTM Standards series.

If using an automated or instrumental method, maintenance and calibration are important. It can be difficult to estimate time and money costs for these items, but there are sources of information available. For maintenance, the manufacturer should be able to provide some estimates. It has been noted that these estimates can be somewhat optimistic. Another source may be others who are or who have used the instrument. Experience can be an accurate, if time consuming, instructor. There may even exist previous in-house maintenance records that will provide valuable information.

For calibration requirements, again the manufacturer should provide some estimates. However, there may be legal requirements such as those specified in the appendixes to 40 CFR 58 detailing minimum requirements for PSD or SIP monitoring. Calibration guidance is also contained in "Quality Assurance Handbook for Air Pollution Measurement Systems, Volumes I and II, [EPA-600/9-76-005 (Vol. I) and EPA-600/4-77-027a (Vol. II)]. The time requirements for calibration and the frequency of audits may vary as in-house records establishing performance are developed. For example, with a new instrument, calibration may be weekly for the first 3 months; then biweekly with weekly audits; and finally monthly with biweekly audits as performance parameters are documented for that particular instrument. Of course, detailed records of maintenance and calibration must be maintained.

Siting

Having established "why," "how," and "what," the next step in designing the sensor system is "where." This topic involves properly siting the sensor to collect representative data. Since 1975, the EPA has issued several documents detailing a procedure for selecting the proper site for a pollutant for different purposes. By following the procedure outlined in these documents, it is possible to logically select a proper site for a particular purpose and to clearly document the procedure followed. This allows for a subsequent audit or review of the site selection process to react to changing conditions without having to duplicate earlier work. The documents available are:

"Selecting Sites for Carbon Monoxide Monitoring."
September 1975. EPA-450/3-75-077.

"Optimum Site Exposure Criteria for SO_2 Monitoring."
April 1977. EPA-450/3-77-013.

"Selecting Sites for Monitoring Total Suspended Particulates."
June 1977. EPA-450/3-77-018.

"Site Selection for the Monitoring of Photochemical Air Pollutants."
April 1978. EPA-450/3-78-013.

All of these siting documents follow the same approach. First the needs or uses of the data are identified, then these uses are coordinated with specific program objectives. After these steps, a flow chart is developed for each siting objective.

It should also be noted that each siting case may be unique and the "proper site" is not necessarily an absolute, fixed item. Given the same background information and a similar siting objective, two "experts" may arrive at different site locations. Often there is a lack of needed information, and even under the best of conditions, siting sensors involves the abstract correlation of large amounts of chemical, meteorological, geographical, and political information. There are no "instant experts" or short cuts to actual experience. However, by following a set of logical procedures, it is possible to arrive at a site location that will adequately meet the program objectives and allow for concise documentation of the selection process. This is important especially in view of the proposed revision to the ambient monitoring regulations.

Section 40 CFR§58.20 requires an annual review of each surveillance network. These changes to the EPA monitoring regulations were promulgated May 10, 1979. In addition to organizing and revising almost all of the EPA ambient monitoring regulations into one section of the Code of Federal Regulations, there is also siting and network design guidance contained in Appendix D of these regulations. The guidance in Appendix D is consistent, both in approach and content, with that contained in the individual siting documents. The documents contain more detail and greater depth than is possible in the regulations.

The location of the sensor is only part of the answer to the where of monitoring. Besides locating the sensor, it is also important to obtain a correct probe location. The location of the probe depends on the chemistry of the specie sampled and, of course, the monitoring objectives. Guidance on probe location is contained in the siting documents and also in Appendix E of 40 CFR§58. By adopting a uniform probe location for each pollutant, comparison of the data from different projects and times is simplified. As mentioned earlier for sensor location, the probe location may vary for each pollutant and each objective. The final choice would represent an optimal compromise between needs and resources.

As part of our network design system, we have specified the why, how, what, and where of our sensor package and network. There are two remaining systems of the data subsystem to define: the recording and transmission system, and the data processing system. Both of these systems are concerned with the collection and processing of the data or signals produced by the sensor systems, and there is some overlapping. It is important to spend time on properly planning each of these, as a great deal of resources have been expended needlessly in these areas. We will work with each separately.

Data Recording

The first part of this subsystem concerns data recording. We may have an electrical signal from one or more instruments from one or more locations, or a set of analytical results from manual methods. In either case, the data must be recorded. If we have an electrical output from an analyzer, several choices are available. We can manually read a meter and record data, use a strip chart recorder, record on punch cards or paper tape, or record on machine-readable magnetic tape or discs. When designing data systems, the major problem is usually optimizing man and machine interactions. In some cases you may have excess manpower and little automation, while the opposite may be true in other cases. Therefore, the first step in this process is to identify the needs. Is data required or produced continuously, are all outputs from analyzers matched, is there a mix of manual and automated sensor systems, and finally is the data for immediate or future use? If the data is to be used for a daily Pollutant Standards Index or to operate a Supplemental Control System, there may be a need for automated recording and processing. However, if the data is to be used for annual trend reports, monthly strip charts may be the best choice.

With the needs identified, resources available should be assessed. This assessment allows a realistic data system to be designed. The goal here again should be to meet the program requirements while minimizing costs. Too often overly elaborate systems have been designed with no consideration of needs. Needs must be prioritized, separating necessary items from desirable, but less essential components. The total mix of components in a system must also be accounted for in the design. If grounding and interface problems exist, it may be advantageous to solve these separately and use one data logger for each station rather than separate strip charts or other separate recorders. Unfortunately, no hard and fast rules exist to assist in making these decisions. Advice should be sought from competent systems engineers or other personnel familiar with the equipment involved.

Data Transmission

The same situation exists for the transmission part of this subsystem. It is important not to overdesign the system and thus waste resources. In reviewing the data needs, speed of utilization must be determined. If it arrives quickly, but is not going to be processed for a month, a simpler system may be more cost effective. The best rule to follow is to make it as simple, cheap, and uncomplicated as is feasible. The choice between on-site pickup of data versus telemetered data will be based on data needs, resources available, and the existing network. Signal conditioning must be designed by a competent electrician to avoid later problems.

Data processing comprises the final part of the Data System. The data processing system involves the selection of a format, validation, analysis, storage, and retrieval. A format is simply a systematic listing of the data recorded. The format chosen should be clearly defined and well documented. This prevents the problem of reconciling incompatible formats later, a process that can be extremely expensive. If the data is to be submitted to another office, identical formats would be desirable. If no standard format exists, a logical, easily understood format should be designed. The EPA has available a computer program, the Comprehensive Data Handling System, which processes aerometric data and puts it into acceptable EPA (SAROAD) format. This software program is offered free to governmental agencies and for a nominal copying charge (<$100) to others from:

National Air Data Branch
OAQPS/MDAD (MD-14)
U.S. Environmental Protection Agency
Research Triangle Park, N.C. 27711

Data Validation

After choosing a format to use for the data that provides a copy, validation can begin. The validation should be performed by an air pollution professional with intimate knowledge of the sensors, recording system, transmission system, as well as any peculiarities of the air pollution problem in the area. This validation should be performed at the lowest level possible to permit the maximum possible recovery of valid data. For example, if there is a two week period in a month's data that has values three times the "normal" values, several possibilities exist. The data may have been analyzed by a substitute while the usual person was on vacation and a factor of three may have been dropped from the denominator of an equation; the instrument may have malfunctioned; meteorological conditions (poor dispersion, stable atmosphere, low mixing depth) may have resulted in increased concentrations. Obviously, in the first case the data can be corrected by including the factor and recomputing; in the second case the data probably will have to be invalidated unless an accurate correction factor can be determined; and in the third case, the data is correct. Only an air pollution professional would recognize the difference, and the closer that person is to the network, the less expensive this process will be. Computer validation is possible to identify outliers, or abnormal values, but manual checking is needed to perform final validation.

Data Analysis

After the data has been formated and validated, the final analysis can be performed. Depending on the nature of the data and the final data use, a variety of statistical procedures exist. These techniques and their use with aerometric data are complex and a professional statistician should be consulted. The type of analysis may be dictated by the standard (requiring arithmetic or geometric means), or the data (long term trends represented by log-normal distributions). Advice from a statistician can help prevent erroneous conclusions.

Storage of the data and/or the samples should prevent physical deterioration, provide a logical system, and should be secure to provide a legal chain of custody. If using thermally sensitive chart paper, storage in a warehouse subject to elevated daytime temperatures would prove problematic and soon the records would be uniformly gray. A logical system provides continuity and, along with a secure storage area and sign-off sheets, helps establish a legal chain of custody for records.

The storage system should not, however, prevent easy access to the data by the proper personnel. Retrieval procedures should not be overly complex, yet must provide a systematic procedure ensuring data security. In automated systems, provisions can be made to restrict access with confidential identification codes or restricted data discs.

After designing the sensor and data subsystems, one final item requiring allocation of resources exists. This is to incorporate a comprehensive quality control program to assure the data produced is correct. Guidance on these programs is contained in the Quality Assurance Handbooks mentioned earlier and in Appendixes A and B of 40 CFR§58. Without adequate quality control of each subsystem, the question of ultimate data validity may be impossible to answer.

References

1. Ball, R. J., and Anderson G. E. *Optimum Site Exposure Criteria for* SO_2 *Monitoring*. EPA-40/3-77-013, US EPA, RTP, NC, 1977.

Chapter 10

Statistical Techniques Employed in Atmospheric Sampling

Introduction

Proper use of statistics and statistical techniques is necessary for evaluating air pollution data. This chapter serves as an introduction to statistics and statistical concepts. Topics to be discussed include: (a) Measures of Central Tendency; (b) Measures of Dispersion; (c) Distribution Curves; and (d) Data Plotting. Although the above topics are not simple, they can be understood and used by nonstatisticians. If a detailed statistical analysis of data is required, it is recommended that an experienced statistician be consulted.

Data Plotting

Data is usually unmanageable in the form in which it is collected. In this section we shall consider the graphical techniques of summarizing such data so that the meaningful information can be extracted from it. Basically there are two kinds of variables to which we assign data: continuous variables and discrete variables. A continuous variable is one that can assume any value in some interval of values. Examples of continuous variables are weight, volume, length, time and temperature. Most air pollution data are taken from continuous variables. Discrete variables, on the other hand, are those variables whose possible values are integers. Therefore, they involve counting rather than measuring. Examples of discrete variables are the number of sample stations, number of people in a room, and number of times a control standard is violated. Since any measuring device is of limited accuracy, measurements in real life are actually discrete in nature rather than continuous, but this should not keep us from regarding such variables as continuous. When a weight is recorded as 165 pounds, it is assumed that the actual weight is somewhere between 164.5 and 165.5 pounds.

Graphical Analysis

Frequency Tables

Let us consider the set of data in Figure 10-1 which represents SO_2 levels for a given hour for 25 days. As a first step in summarizing the data from Figure 10-1, we would form a frequency table as shown in Figure 10-2.

Days	SO_2 Concentration (ppb)*
1	53
2	72
3	59
4	45
5	44
6	85
7	77
8	56
9	157
10	83
11	120
12	81
13	35
14	63
15	48
16	180
17	94
18	110
19	51
20	47
21	55
22	43
23	28
24	38
25	26

*ppb = parts per billion collected SO_2 levels

Figure 10-1. SO_2 levels.

Class Interval (ppb)	Frequency of Occurrence
25 – 40	4
40 – 55	7
55 – 70	4
70 – 85	4
85 – 100	2
100 – 115	1
115 – 130	1
130 – 145	0
145 – 160	1
160 – 175	0
175 – 190	1

Figure 10-2. Frequency table.

In constructing the frequency table it can be seen that we have divided the data into 11 class intervals with each interval being 15 units in length. The choice of dividing the data into 11 intervals was purely arbitrary. However, in dealing with data it is a rule of thumb to choose the length of the class interval such that 8-15 intervals will include all of the data under consideration. Deriving the frequency column involves nothing more than counting the number of values in each interval.

From observation of the frequency table, we can now see the data taking form. The values appear to be clustered between 25 and 85 ppb. In fact, nearly 80 percent are in this interval.

The Frequency Polygon

As a further step we can graph the information in the frequency table. One way of doing this would be to plot the frequency midpoint of the class interval. The solid line connecting the points of Figure 10-3 forms a frequency polygon.

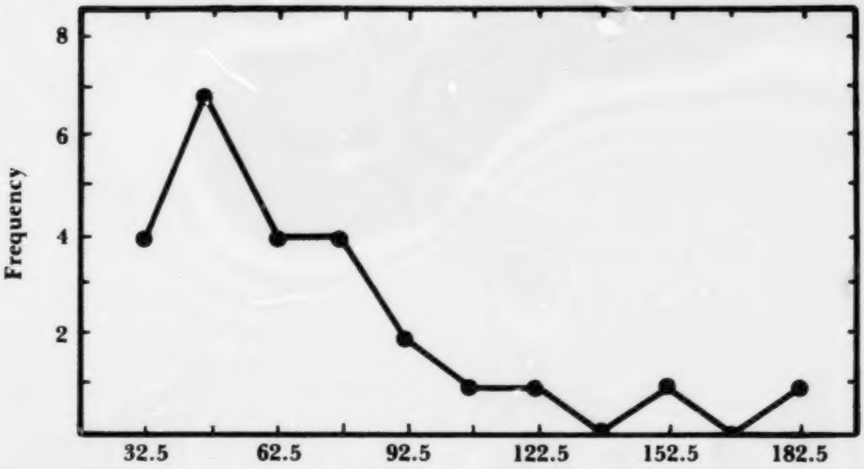

Figure 10-3. Pollution concentration (mid-point of class interval) frequency polygon.

The Histogram

Another method of graphing the information would be by constructing a histogram as shown in Figure 10-4. The histogram is a two-dimensional graph in which the length of the class interval is taken into consideration. The histogram can be a very useful tool in statistics especially if we convert the given frequency scale to a relative scale so that the sum of all the ordinates equals one. This is shown in Figure 10-5. Thus, each ordinate value is derived by dividing the original value by the number of observations in the sample, in this case 25. The advantage in constructing a histogram like the one in Figure 10-5 is that we can read probabilities from it, if we can assume a scale on the abscissa such that a given value will fall in any one interval is the area under the curve in that interval. For example, the probability that a value will fall between 55 and 70 is equal to the area under the curve in that interval, which is 0.16 × 1 = 0.16.

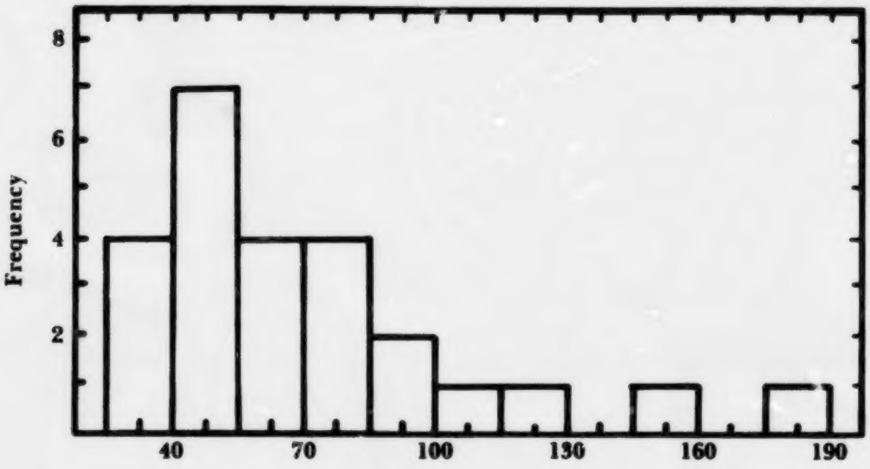

Figure 10-4. Pollutant concentration histogram of frequency distribution curve.

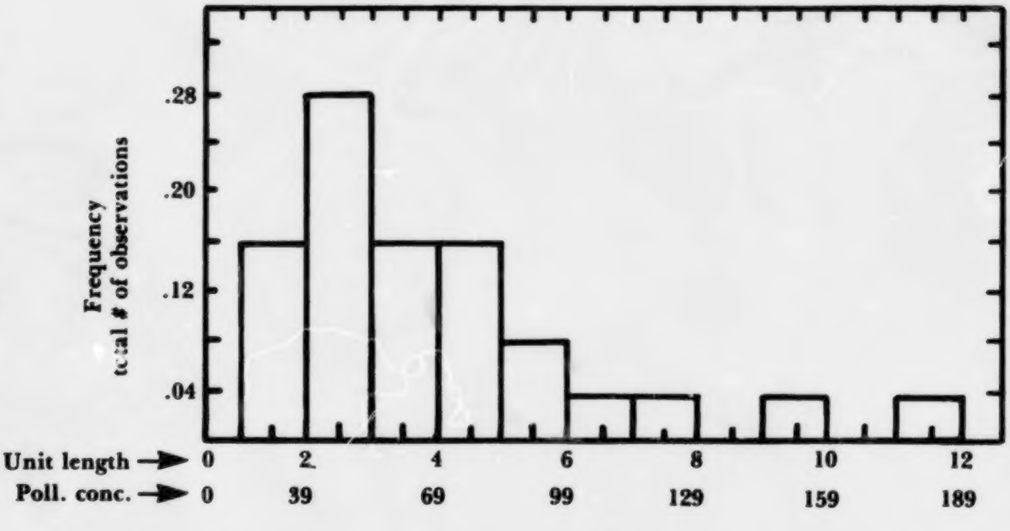

Figure 10-5. Histogram of percent frequency distribution curve.

The Cumulative Frequency Distribution

From the frequency table and histogram discussed above we can construct a cumulative frequency table and curve as shown in Figures 10-6 and 10-7.

SO_2 level	Frequency	Relative frequency less than a given value
Under 40	4	.16
" 55	11	.44
" 70	15	.60
" 85	19	.76
" 100	21	.84
" 115	22	.88
" 130	23	.92
" 145	23	.92
" 160	24	.96
" 175	24	.96
" 190	25	1.00

Figure 10-6. Cumulative frequency table.

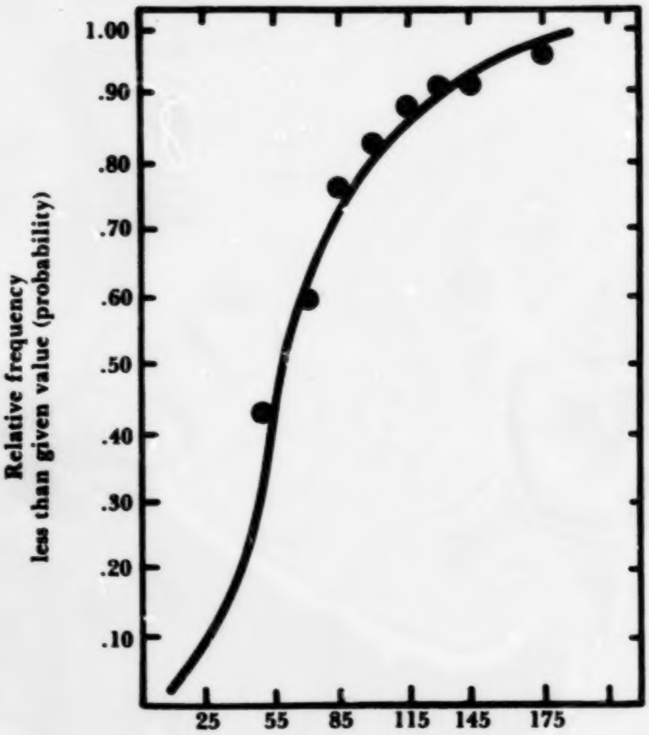

Figure 10-7. Cumulative frequency distribution curve.

The cumulative frequency table gives the number of observations less than a given value. Probabilities can be read from the cumulative frequency curve. For example, to find the probability that a value will be less than 85 we read up to the curve at the point X = 85 and across to the value 0.76 on the Y axis.

Distribution of Data

When we draw a histogram for a set of data we are representing the distribution of the data. Different sets of data will vary in relation to one another and, consequently, their histograms will look different. Basically, there are three characteristics that will distinguish the distributions of different sets of data. These are central location, dispersion, and skewness. These are characterized in Figure 10-8. Curves A and B have the same central location, but B is more dispersed. However, both A and B are symmetrical and are, therefore, said not to be skewed. Curve C is skewed to the right as well as having a different central location than A and B. Mathematical measures of central location and dispersion will be discussed later.

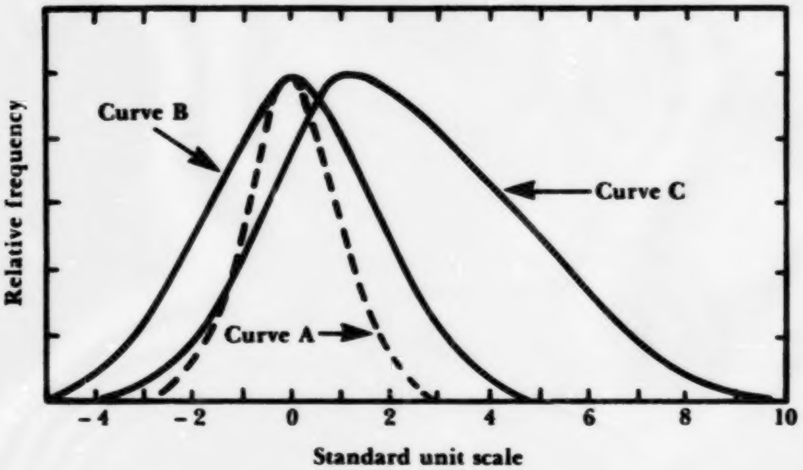

Figure 10-8. Relative frequency distribution showing: Curve A and B both centrally located; Curve B being more disperse than Curve A and the skewness of Curve C.

Transformation of Data

In most statistical work, it is required to have data that closely approximate a particular symmetrical curve called the normal curve. Both curves A and B in Figure 10-8 are examples of normal curves. In dealing with skewed curves, such as C in the same figure, it is desirable to transform the data in some way so that a symmetrical curve resembling the normal curve results. Referring to the frequency table (Figure 10-2) and histogram (Figure 10-4) of the data used earlier, it can be seen that for this set of data the distribution is skewed in the opposite direction as curve C above.

The Logarithmic Transformation

One of the most successful ways of deriving a symmetrical distribution from a skewed distribution is by expressing the original data in terms of logarithms. The logarithms of the original data are given in Figure 10-9.

Day	Pollutant Conc. X	$Log_{10}X$
1	53	1.724
2	72	1.857
3	59	1.771
4	45	1.653
5	44	1.644
6	85	1.929
7	77	1.887
8	56	1.748
9	157	2.196
10	83	1.919
11	120	2.079
12	81	1.909
13	35	1.544
14	63	1.799
15	45	1.681
16	180	2.255
17	94	1.973
18	110	2.041
19	51	1.708
20	47	1.672
21	55	1.740
22	43	1.634
23	28	1.447
24	58	1.580
25	26	1.415

Figure 10-9. Logarithmic transformation.

Arbitrarily dividing the logarithmic data into 9 class intervals each of 0.1 unit in length we can write the logarithmic frequency table in Figure 10-10. As can be seen a frequency plot versus the logarithmic scale would more closely approximate a symmetrical curve than would the arithmetic plot.

Class interval	Tally	Frequency	Cumulative frequency
1.4 – 1.5	11	2	2
1.5 – 1.6	11	2	4
1.6 – 1.7	1111	5	9
1.7 – 1.8	1111 1	6	15
1.8 – 1.9	11	2	17
1.9 – 2.0	1111	4	21
2.0 – 2.1	11	2	23
2.1 – 2.2	1	1	24
2.2 – 2.3	1	1	25

Figure 10-10. Logarithmic frequency table.

Probability Graph Paper

Probability graph paper is used in the analysis of cumulative frequency curves; for example, the graph paper can be used as a rough test of whether the arithmetic or the logarithmic scale best approximates a normal distribution. The scale, arithmetic or logarithmic, on which the cumulative frequency distribution of the data is more nearly a straight line is the one providing the better approximation to a normal distribution. Plotting the cumulative distribution curve of the data above on the two scales, it can be seen that the logarithmic scale yields the better fit (Figure 10-11).

These probability plots can also be used to get estimates of the mean and standard deviation of the data. The estimate of the mean, as will be shown later, is the 50th percentile point, and the estimation of the standard deviation is the distance from the 50th percentile to the 16th percentile.

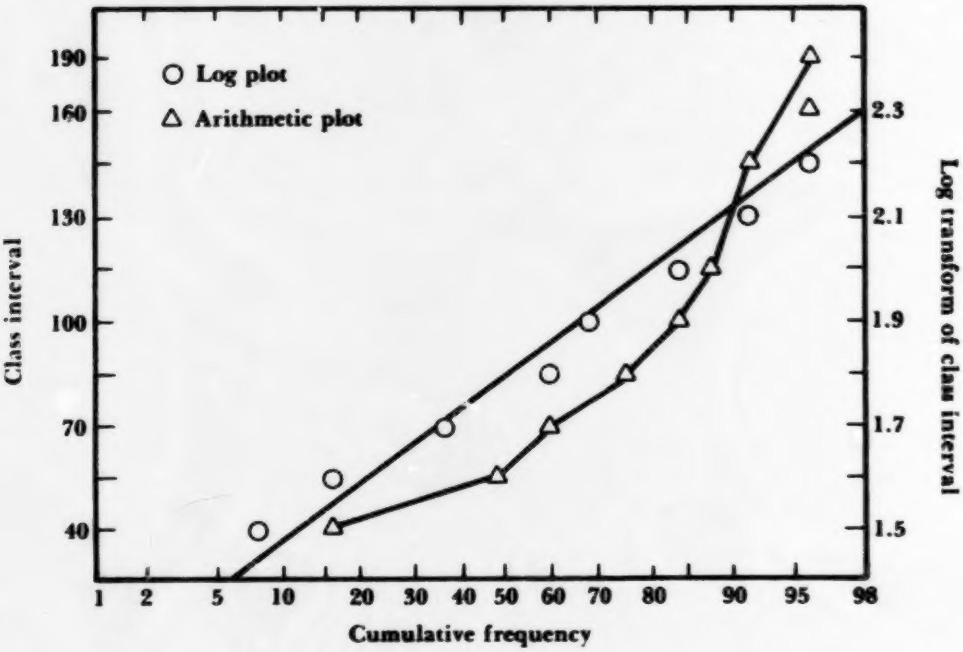

Figure 10-11. Normalized data plot vs. non-transformed data.

Least Squares Linear Regression

If the relationship between two variables is significant, a linear regression line or line of "best fit" may be drawn to represent the data. Algebraically a straight line has the following form

(Eq. 10-1) $$y = mx + b$$

Where:
y = *variable plotted on the ordinate*
x = *variable plotted on abscissa*
b = *y intercept*
m = *slope* = *change in y/change in x*

Linear regression minimizes the vertical distance between all data points and the straight line (see Figure 10-12).

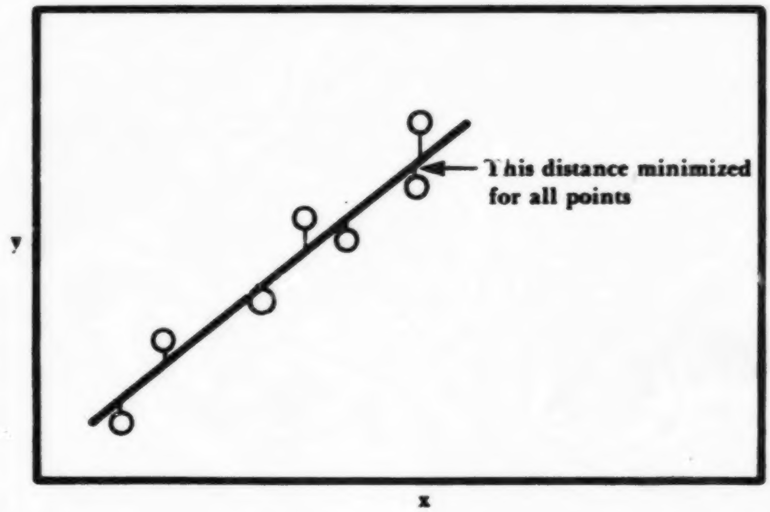

Figure 10-12. Linear regression curve.

The constants *m* and *b* for the "best fit" line can be determined using the following equations:

(Eq. 10-2) $$m = \frac{\Sigma xy - \frac{(\Sigma x)(\Sigma y)}{n}}{\Sigma x^2 - \frac{(\Sigma x)^2}{n}}$$

(Eq. 10-3) $$b = \bar{y} - m\bar{x}$$

Where:
n = *number of observations*
$\bar{y} = \Sigma y/n$; $\bar{x} = \Sigma x/n$

Example Problem

The following data was collected during a calibration of a chemiluminescent NO_x analyzer.

X = Concentration NO_x (ppm)	0.05	0.10	0.20	0.30	0.45
Y = Instrument response (volts)	1.20	2.15	3.90	6.20	9.80

Values for m and b for the "best fit" line can be calculated from Σx, Σy, Σx^2, Σxy, n, $\bar{y}$, and $\bar{x}$.

Solution:

$\Sigma x = 0.05 + 0.10 + 0.20 + 0.30 + 0.45 = 1.1$

$\Sigma y = 1.20 + 2.15 + 3.90 + 6.20 + 9.80 = 23.25$

$\Sigma x^2 = (0.05)^2 + (0.10)^2 + (0.20)^2 + (0.30)^2 + (0.45)^2 = .345$

$\Sigma xy = (0.05)(1.20) + (0.10)(2.15) + (0.20)(3.90) + (0.30)(6.20) + (0.45)(9.80) = 7.33$

$n = 5$

$$\bar{x} = \frac{\Sigma x}{n} = \frac{1.1}{5} = 0.22$$

$$\bar{y} = \frac{\Sigma y}{n} = \frac{23.25}{5} \quad 4.65$$

$$m = \frac{7.33 - \dfrac{(1.1)(23.25)}{5}}{0.345 - \dfrac{(1.1)^2}{5}} = \frac{2.22}{0.103} = 21.6$$

$b = 4.65 - (21.6)(0.22) = -0.102$

The equation for this calibration curve would be

$y = 21.6x - 0.102$

Volts = 21.6 (ppm) − 0.102

Rearranging

$$ppm = \frac{volts + 0.102}{21.6}$$

Measures of Central Tendency

Arithmetic Average or Mean

The most basic way of summarizing data is the computation of a central value. The most commonly used central value statistic is the arithmetic average or the mean. This statistic is particularly useful when applied to a set of data having a fairly symmetrical distribution. The mean is an efficient statistic in that it summarizes all the data in the set, because each piece of data is taken into account in its computation. The formula for computing the mean is

(Eq. 10-4)

$$\bar{X} = \frac{X_1 + X_2 + X_3 \ldots + X_n}{n} = \frac{\sum_{i=1}^{n} X_i}{n} = \frac{\Sigma X_i}{n}$$

Where:
$\bar{X}$ = *arithmetic mean*
X_i = *any individual measurement*
n = *total number of observations*
$X_1, X_2, X_3,$ = *measurements 1, 2, and 3 respectively*

The arithmetic mean is not a perfect measure of the true central value of a given data set. Arithmetic means overemphasize the importance of one or two extreme data points. Many measurements of a normally distributed data set will have an arithmetic mean that closely approximates the true central value.

Median

When a distribution of data is asymmetrical, such as that of Figure 10-13, it is sometimes desirable to compute a different measure of central value. This second measure, known as the median, is simply the middle value of a distribution, that is, the quantity above which half the data lie and below which the other half of the data lie. If n data are listed in their *order of magnitude*, the median is the $[(N+1)/2]$th value. If the number of data is even, then the numerical value of the median is the value midway between the two data nearest the middle. The median, being a positional value, is less influenced by extreme values in a distribution than the mean. The median alone is not a good measure of central tendency.

Example:

Find the median of 22, 10, 15, 8, 13, 18

Solution: The data must first be arranged in order of magnitude such as:

8, 10, 13, 15, 18, 22

Now the median is 14, or the value half way between 13 and 15, since this data set has an even number of measurements.

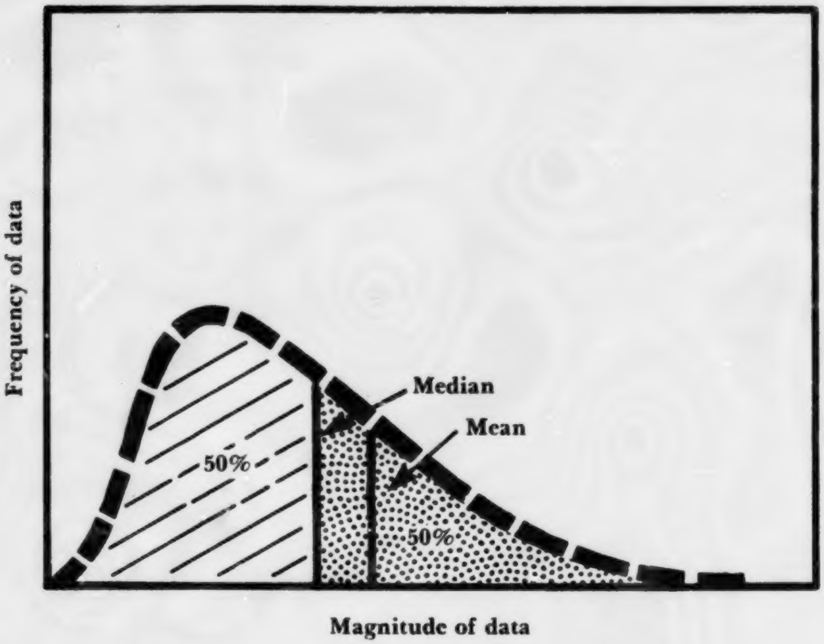

Figure 10-13. Example of nonsymmetrical distribution of data (median vs. mean).

Geometric Mean

Another measure of central tendency used in more specialized applications is the geometric mean ($\overline{X}_g$). The geometric mean can be calculated using the following equation:

(Eq. 10-5)

$$\overline{X}_g = \sqrt[n]{(X_1)(X_2)\ldots(X_n)}$$

If scientific calculators are not available, a formula that more readily lends itself to a four function calculator is

$$Log_{10}\overline{X}_g = \frac{1}{n}\,\Sigma\,Log_{10}X_i$$

The geometric mean is most often used for data whose causes behave exponentially rather than linearly, such as in the growth of bacteria, measurements that are ratios, or lognormal distributions.

In a distribution shaped like that of Figure 10-13, the geometric mean, like the median, will yield a value closer to the main cluster of values than will the mean. The arithmetic mean is always higher than the geometric mean.

Example

Calculate the geometric mean of 3.0, 2.5, 2.2, 3.4, 3.2

Solution:

$$\bar{X}_g = \sqrt[5]{(3.0)(2.5)(2.2)(3.4)(3.2)} = 2.8$$

or

$$Log_{10}\bar{X}_g = \frac{1}{5}(.477 + .398 + .342 + .531 + .505)$$

$$Log_{10}\bar{X}_g = 0.4506$$

$$\bar{X}_g = 2.8$$

Measures of Dispersion

It is, of course, quite possible for two separate distributions of data to have equal means and yet be considerably different. This fact is depicted in Figure 10-14. Distribution A has data that are bunched relatively much closer to the mean than the data of distribution B. Distribution B is said to have greater variability or dispersion than A. Thus, it is apparent that, instead of drawing a diagram each time one wishes to compare distributions, a statistic that measures variability is desirable.

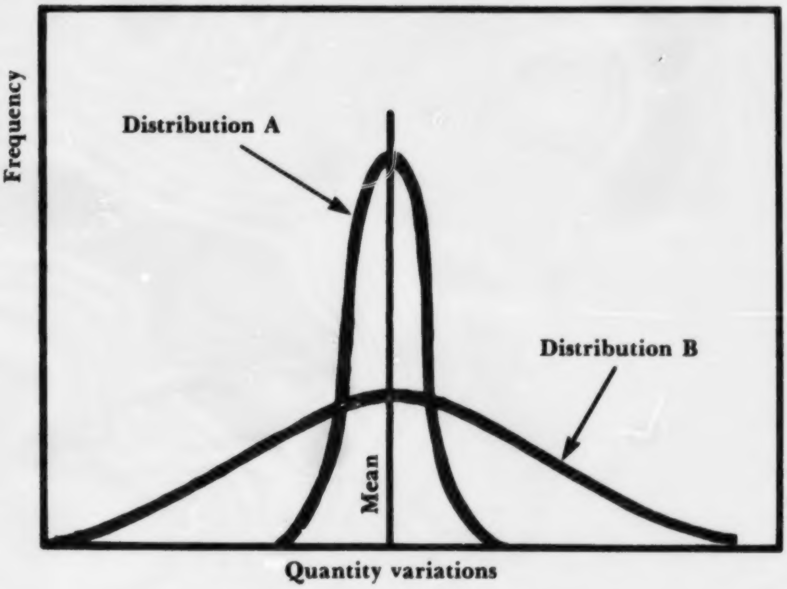

Figure 10-14. Dispersion characteristic curves.

Standard Deviation

The most commonly used measure of dispersion, or variability, of sets of data is the standard deviation. Its defining formula is given by the expression:

(Eq. 10-6)

$$s = +\sqrt{\frac{\Sigma(X_i - \overline{X})^2}{n-1}}$$

Where: s *= the standard deviation (always positive)*
X_i *= a datum value*
$\overline{X}$ *= the mean of the data sample*
n *= the number of observations*

The expression $(X - \overline{X})$ shows that the deviation of each piece of data from the mean is taken into account by the standard deviation.

Although the defining formula for the standard deviation gives insight into its meaning, this algebraically equivalent formula makes computation much easier:

$$s = +\sqrt{\frac{n\Sigma X_i^2 - (\Sigma X_i)^2}{n(n-1)}}$$

When using this formula, it is only necessary to array the data in a column, construct another column of squared data, and find the sums for both columns. (Note that ΣX^2 does not equal $(\Sigma X)^2$).

Suppose one wishes to compute the mean and standard deviation of 220 data points. After the computation, it is found that one of the data points has been omitted. Unless the omitted value exactly equals the obtained mean, the mean of the complete set of data will be different from the one obtained; therefore, the deviations of the data from the mean will all be changed, and will necessitate untold additional laborious computation. But with the computational formula for s, it is only necessary to add the omitted value to the X column and its square to the X^2 column and plug the corrected values into the computational formula. The computational formula is also handy for desk calculators, as they are designed to keep running totals of numbers and their squares simultaneously. Also, no errors inherent in the computation are introduced, as when one obtains a mean such as 3.333.

The Range

Despite the existence of a computational formula for the standard deviation, the easiest way to obtain a measure of dispersion of a set of data is to find the difference between the maximum and the minimum values in the set. This simple measure is appropriately termed the range. Obviously the range does not make full use of the information contained in the data, since only two of the data points are taken into account. The range is, however, reasonably efficient compared to s when the number of data is 10 or less. Thus the range is an extremely handy measure of variability for small samples.

Standard Geometric Deviation

Dispersion of skewed data such as lognormal distributions is better measured by the standard geometric deviation. The standard geometric deviation is very similar to the standard deviation. The dispersion in the log of the measurements is measured by the geometric standard deviation instead of the dispersion of the measurements. The log calculation normalizes the data to better approximate a normal distribution. The formula for calculating the standard geometric deviation is:

(Eq. 10-7)

$$s_g = antilog \left[\frac{\Sigma(logX - \overline{logX})^2}{n-1} \right]^{1/2}$$

The following formula is mathematically identical, yet it is much easier to use in calculation:

$$s_g = antilog \left[\frac{\Sigma(logX)^2 - \frac{(\Sigma logX)^2}{n}}{n-1} \right]^{1/2}$$

Distribution Curves

Many types of distribution curves exist; binomial, t, chi, F, normal, and lognormal are just a few of the existing distributions. However, in air pollution measurements, the normal and lognormal are the most commonly occuring ones. Thus only these two will be discussed.

The Normal Distribution

One reason the normal distribution is so important is that a number of natural phenomena are normally distributed or closely approximate it. In fact many experiments when repeated a large number of times will approach the normal distribution curve. In its pure form, the normal curve is a continuous, symmetrical, smooth curve shaped like the one shown in Figure 10-15. Naturally, a finite distribution of discrete data can only approximate this curve. The normal curve has the following definite relations to the descriptive measures of a distribution.

The Mean and Median

The normal distribution curve is symmetrical; therefore, both the mean and the median are always to be found in the middle of the curve. Recall that in general the mean and median of a nonsymmetrical distribution do not coincide.

The Range

The normal curve ranges along the x axis from minus infinity to plus infinity. Therefore, the range of a normal distribution is infinite.

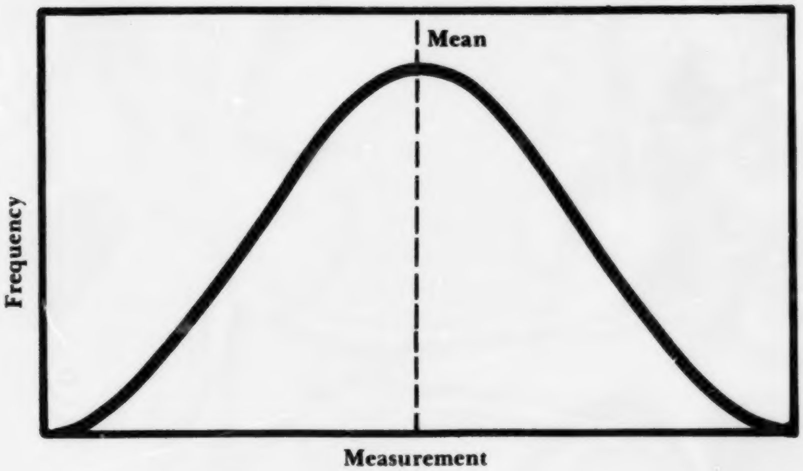

Figure 10-15. Gaussian distribution curve "normal curve".

The Standard Deviation

The standard deviation (s) becomes a most meaningful measure when related to the normal curve. A total of 68.2 percent of the area lying under a normal curve is included by the part from one standard deviation below to one standard deviation above the mean. A total of 95.4% lies −2 to +2 standard deviations from the mean (see Figure 10-16). By using tables found in statistics texts and handbooks, one can determine the area lying under any part of the normal curve.

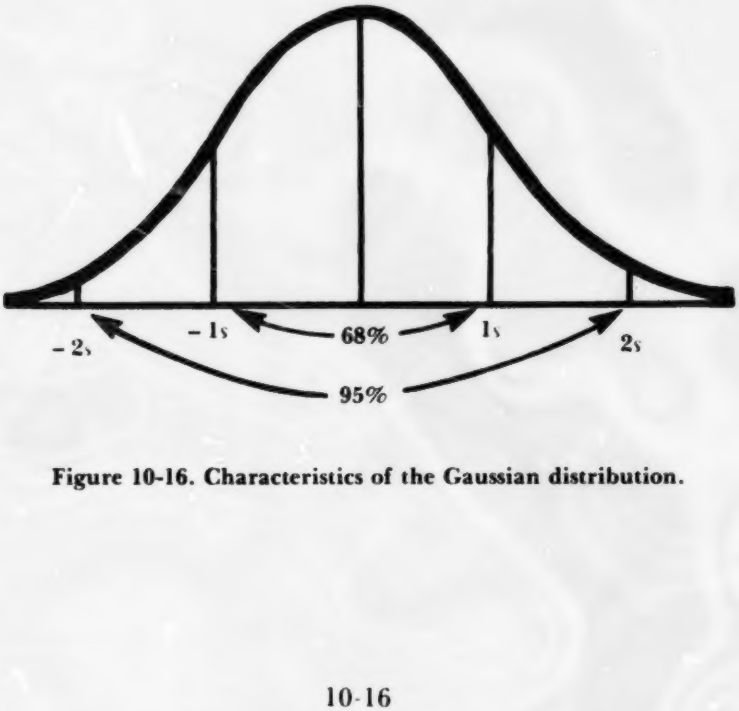

Figure 10-16. Characteristics of the Gaussian distribution.

These areas under the normal distribution curve can be given probability interpretations. For example, if an experiment yields a nearly normal distribution with mean equal to 30 and standard deviation of 10, we can expect about 68% of a large number of experimental results to range from 20 to 40, so that the probability of any particular experimental result's having a value between 20 and 40 is about 0.68.

Applying the properties of the normal curve to the testing of data readings one can determine whether a change in the conditions being measured is shown or whether only chance fluctuations in the readings are represented. For a well-established set of criterion data, a frequently used set of control limits is plus and minus three standard deviations. That is, a special investigation of data readings trying these limits can be used to determine whether the conditions under which the original data were taken have changed. Since the limits of three standard deviations on either side of the mean include 99.7 percent of the area under the normal curve, it is very unlikely that a reading outside these limits is due to the conditions producing the criterion set of data. The purpose of this technique is to separate the purely chance fluctuations from the other causes of variation. For example, if a long series of observations of an environmental measurement yield a mean of 50 and a standard deviation of 10, then control limits will be set up as 50 plus and minus 30, in other words, plus and minus three standard deviations, or from 20 to 80. So, a value of 80 would suggest that the underlying conditions have changed, and that a large number of similar observations at this time would yield a distribution of results with a mean different (larger) than 50.

This process of determining whether a value represents a significant change is closely related to the use of control charts. Often in setting up control limits it is necessary to divide the available data into subgroups and calculate the mean and standard deviations of each of these groups, making careful note of the conditions prevailing under each subgroup. In collecting data to establish control limits, the time sequence can be important, for the data in a time series may reveal some non-random patterns. It is apparent that as much information as possible should be gathered about the causes and conditions in effect during the period of obtaining a criterion set of data. Generally the conditions during this period should be "normal" or as much in control as possible.

In the situation where one takes readings of some environmental quantity, the appearance of data beyond the control limits might suggest the starting of a new data grouping to further ascertain whether the underlying environmental variable has changed.

It should be kept in mind that the limits of plus and minus three standard deviations are traditional rather than absolute. They have been found through experience to be very useful in many control situations, but each experimenter must decide what limits would be most suitable for a given purpose by determining what levels of probability would be needed to quantify acceptance and rejection bounds.

Lognormal Distributions

Lognormal distributions can best be demonstrated by means of an example.

If hourly sulfur dioxide concentrations are plotted against frequency of occurrence, as in Figure 10-15, a skewed distribution would exist similar to the one in Figure 10-17. Such a curve indicates that many concentrations are close to zero and that few are very high. Unlike temperature, or wind direction, sulfur dioxide concentrations are blocked on the left because values less than zero do not exist. Because numerous aids exist for normal distributions it is desirable to normalize this type of distribution. By plotting the log of hourly SO_2 concentrations against the frequency of occurrence, a "bell-shaped" curve similar to Figure 10-15 is obtained. By making this simple normalizing feature, all existing normal distribution tables can be used to make probability interpretations.

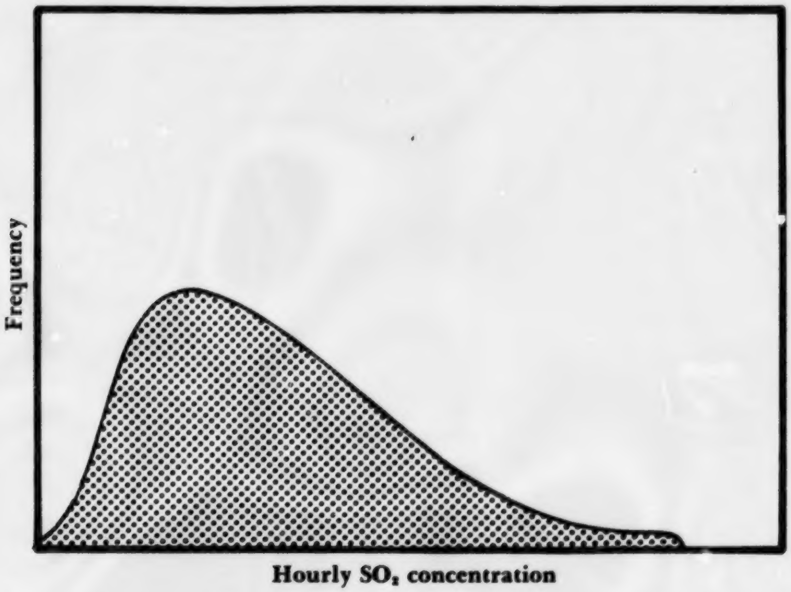

Figure 10-17. Frequency vs. concentration of SO_2.

References & Extra Reading

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Appendixes

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A1

Appendix 1

Theory and Calibration Procedures for the Use of a Rotameter

Nomenclature

A_f = cross sectional area of the float

A_m = annular area between the circumference of the float and the inside circumference of the meter tube at that position

C = drag coefficient

C_m = length which is characteristic of the physical system under study (used to calculate Reynold's Number)

d = length which is characteristic of the physical system under study

D_f = diameter of the float

D_t = diameter of the tube at the float position

g = local acceleration due to gravity

g_c = dimensional constant

m_f = mass of the float

M_m = molecular weight of the metered gas

M_1, M_2, M_3. . .etc. = value of molecular weight of the metered gas at conditions 1, 2, 3. . .etc.

N_{Re} = Reynold's Number

N_{Re}/C_m = dimensionless factor defined by equation 14

P_m = absolute pressure of the metered gas

P_1, P_2, P_3. . .etc. = values of absolute pressure at conditions 1, 2, 3. . .etc.

Q_m = volumetric flow rate through the meter at conditions of pressure (P_m), temperature (T_m), and molecular weight (M_m)

R = universal gas constant

T_m = absolute temperature of the metered gas

T_1, T_2, T_3. . .etc. = values of absolute temperature at conditions 1, 2, 3. . .etc.

ν = average gas velocity through the annual area of the meter

V_f = volume of the float

μ = viscosity of flowing fluid (used to calculate Reynold's Number)

μ_m = viscosity of the metered gas

ϱ = density of flowing fluid (used to calculate Reynold's Number)

ϱ_f = density of the float

ϱ_m = density of the metered gas

Description of a Rotameter

The rotameter (Figure A-1) is a variable area meter which consists of a vertical, tapered, transparent tube containing a float. The float moves upward as the fluid flow increases. A variable ring or annulus is created between the outer diameter of the float and the inner wall of the tube. As the float moves upward in the tube, the area of the annulus increases. The float will continue to move upward until a pressure drop across the float which is unique for each rotameter is reached. This pressure drop across the float is constant regardless of the flow rate. Graduations are etched on the side of the tube so that an instantaneous reading may be observed.

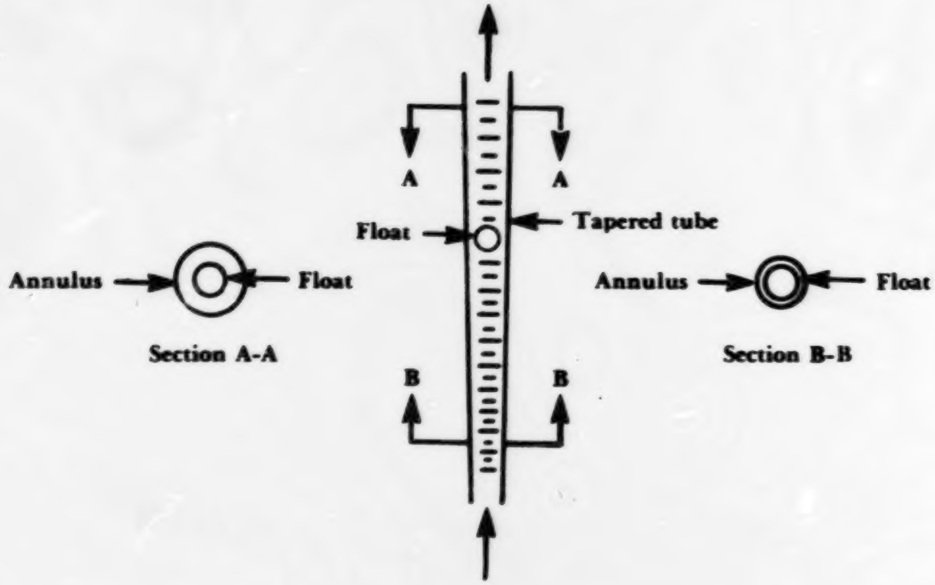


Figure A-1. Rotameter

Development of Flow Equations

General Flow Rate Equations

A free body diagram of the forces acting upon the rotameter float is shown in Figure A2. The weight of the float is equal to the force of gravity acting on the float. The buoyant force is equal to the weight of the gas that is displaced by the float. The drag force is equal to the frictional forces acting between the float and the moving gas stream. Mathematically these forces are as follows:

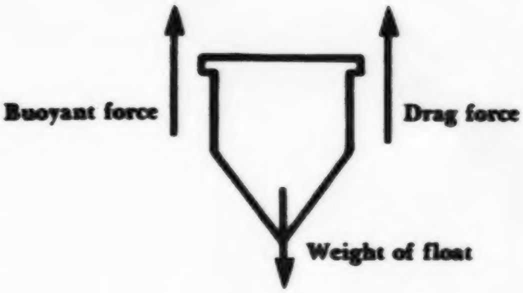


Figure A-2. Forces acting upon a rotameter float.

$$\text{Drag force} = \frac{C A_f \rho_m v^2}{2 g_c}$$

$$\text{Weight of float} = \frac{V_f \rho_f g}{g_c}$$

$$\text{Buoyant force} = \frac{V_f \rho_m g}{g_c}$$

Where: A_f = *cross sectional area of the float*
C = *drag coefficient*
g = *local acceleration due to gravity*
g_c = *dimensional constant*
v = *average gas velocity through the annular area of the meter*
V_f = *volume of the float*
ρ_f = *density of the float*
ρ_m = *density of the metered gas*

When the forces acting in an upward direction exactly equal the force acting in a downward direction the float will remain stationary in the tube. Equating these forces yields:

$$\frac{C A_f \rho_m v^2}{2 g_c} + \frac{V_f \rho_m g}{g_c} = \frac{V_f \rho_f g}{g_c}$$

Cancelling like terms (g_c) and rearranging yields:

$$V_f \rho_f g - V_f \rho_m g = \frac{C A_f \rho_m v^2}{2}$$

Solving for v and factoring out V_f and g from the first two terms yields:

(Eq. A-1)
$$v = \left[\frac{2V_f\, g(\varrho_f - \varrho_m)}{CA_f\varrho_m}\right]^{1/2}$$

The area of the float is equal to $\pi D_f^2/4$ where D_f is the diameter of the float. Substituting $\pi D_f^2/4$ for A_f in Equation A-1 yields:

(Eq. A-2)
$$v = \left[\frac{8V_f\, g(\varrho_f - \varrho_m)}{C\pi D_f^2\varrho_m}\right]^{1/2}$$

Let C_m equal $(8/C\pi)^{1/2}$ where C_m is called a meter coefficient and is dependent upon the drag coefficient. Substituting C_m for $(8/C\pi)^{1/2}$ in Equation A-2 yields:

(Eq. A-3)
$$v = C_m\left[\frac{V_f\, g(\varrho_f - \varrho_m)}{D_f^2\varrho_m}\right]^{1/2}$$

Because the drag coefficient C is dependent upon Reynold's Number, C_m must also be a function of Reynold's Number. Because the density of the gas flowing in the rotameter is very small compared to the density of the float, it can be ignored in the $(\varrho_f - \varrho_m)$ term. Modifying the $(\varrho_f - \varrho_m)$ term in Equation A-3 yields:

(Eq. A-4)
$$v = C_m\left[\frac{V_f\, g\varrho_f}{D_f^2\varrho_m}\right]^{1/2}$$

The volumetric flow rate (Q_m) through the rotameter is equal to the product of the velocity (v) and the annular area of the meter (A_m). Substituting Q_m/A_m for v in Equation A-4 yields:

$$\frac{Q_m}{A_m} = C_m\left[\frac{V_f\, g\varrho_f}{D_f^2\varrho_m}\right]^{1/2}$$

Rearranging terms and removing D_f^2 from the radical yields:

(Eq. A-5)
$$Q_m = \frac{C_m A_m}{D_f}\left[\frac{V_f\, g\varrho_f}{\varrho_m}\right]^{1/2}$$

The density of the float ϱ_f is equal to the mass of the float (m_f) divided by the volume of the float. Substituting m_f/V_f for ϱ_f in Equation A-5 and cancelling the V_f's yields:

(Eq. A-6)
$$Q_m = \frac{C_m A_m}{D_f}\left[\frac{gm_f}{\varrho_m}\right]^{1/2}$$

The density of the gas mixture passing through the meter (ϱ_m) is equal to $P_m M_m / R T_m$ where P_m is the absolute pressure at the meter, M_m is the apparent molecular weight of the gas mixture passing through the meter, R is the universal gas constant, and T_m is the absolute temperature of the gas mixture. Substituting $P_m M_m / R T_m$ for ϱ_m in Equation A-6 yields the general flow rate equation for a rotameter:

(Eq. A-7)
$$Q_m = \frac{C_m A_m}{D_f} \left(\frac{g m_f R T_m}{P_m M_m} \right)^{1/2}$$

Computation of Reynold's Number

Reynold's Number is defined as $\nu d \varrho / \mu$ where ν is the velocity flow, d is a length which is characteristic of the physical system under study, ϱ is the density of the flowing fluid, and μ is the viscosity of the flowing fluid. When calculating Reynold's Number for a gas flowing through a rotameter, the length characteristic of the physical system (d) is the difference between the tube diameter (D_t) and the diameter of the float (D_f). Therefore, Reynold's Number may be calculated by using the following equation:

(Eq. A-8)
$$N_{Re} = \frac{\nu (D_t - D_f) \varrho}{\mu}$$

The average velocity of flow through the rotameter is given by Q_m / A_m where Q_m is the volumetric flow rate through the meter and A_m is the annular area between the inside circumference of the tube at the float position.

Substituting Q_m / A_m for ν in Equation A-8 yields:

(Eq. A-9)
$$N_{Re} = \frac{Q_m (D_t - D_f) \varrho}{A_m \mu}$$

The density of the flowing fluid ϱ is equal to $P_m M_m / R T_m$ where P_m is the absolute pressure of the metered gas, M_m is the apparent molecular weight of the metered gas, R is the universal gas constant, and T_m is the absolute temperature of the metered gas.

Substituting $P_m M_m / R T_m$ for ϱ in Equation A-9 yields:

(Eq. A-10)
$$N_{Re} = \frac{Q_m (D_t - D_f) P_m M_m}{A_m \mu R T_m}$$

Adding the subscript m to the viscosity term μ in Equation A-10 to denote the viscosity of the metered gas yields the following equation which is used to calculate Reynold's Number for gas flow in a rotameter.

(Eq. A-11)
$$N_{Re} = \frac{Q_m (D_t - D_f) P_m M_m}{A_m \mu_m R T_m}$$

Common Practices in the Use of a Rotameter for Gas Flow Measurement

It can be seen from Equation A-7 that the volumetric flow rate through a rotameter can be calculated when such physical characteristics as the diameter and the mass of the float and the annular area of the meter at each tube reading are known providing measurements are made of the temperature, pressure and molecular weight of the metered gas. Before these calculations of the volumetric flow rate can be made, data must be known about the meter coefficient C_m. The meter coefficient being a function of Reynold's Number is ultimately a function of the conditions at which the meter is being used. To obtain data on the meter coefficient, the meter must be calibrated. However, because of the ease involved in using calibration curves, common practice is to use calibration curves to determine volumetric flow rates instead of calculating the flow rates from raw data.

Procedures for the Calibration of a Rotameter

A common arrangement of equipment for calibrating a rotameter is shown in Figure A-3.

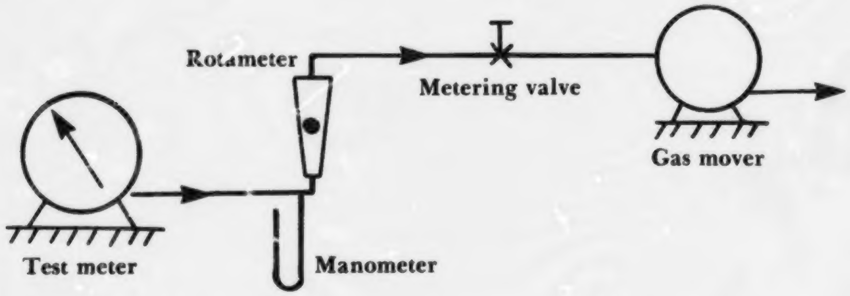


Figure A-3. Test setup for calibrating a rotameter.

Flow through the calibration train is controlled by the metering valve. At various settings of the rotameter float, measurements are made of the flow rate through the train and of the pressure and temperature of the gas stream at the rotameter. The temperature of the gas stream is usually assumed to be the same as the temperature of the ambient air. If the test meter significantly affects the pressure or temperature of the gas stream, measurements should also be made of the actual pressure and temperature at the test meter. A typical rotameter calibration curve is illustrated in Figure A-4.

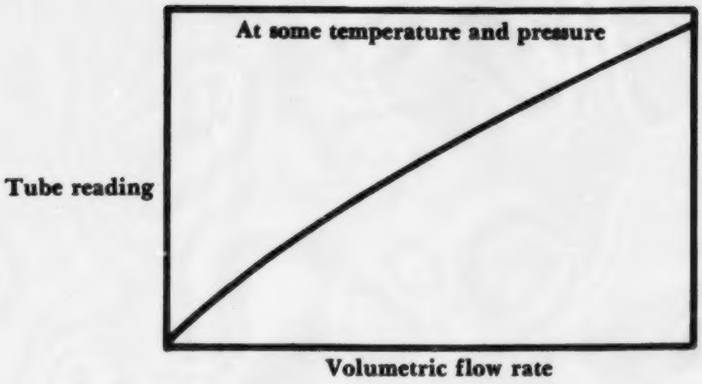


Figure A-4. Rotameter calibration curve.

To make the calibration curve useful, the temperature and pressure of the volumetric flow rate must be specified.

A Universal Calibration Curve

The normal arrangement of the components in a sampling train is shown in Figure A-5. Since the meter is usually installed downstream from the pollutant collector, it can be expected to operate under widely varying conditions of pressure, temperature, and molecular weight. This requires a different calibration curve for each condition of pressure, temperature, and molecular weight. This can be facilitated by drawing a family of calibration curves, which would bracket the anticipated range of pressures, temperatures and molecular weights, as shown in Figure A-6.

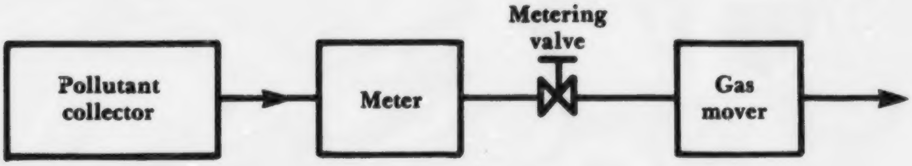


Figure A-5. Arrangement of sampling components.

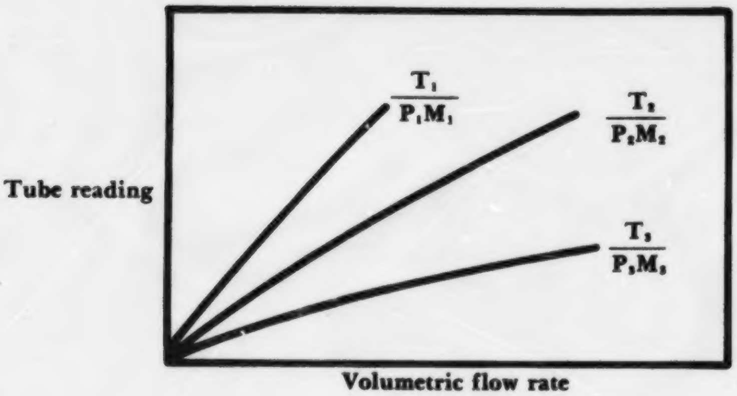


Figure A-6. Family of rotameter calibration curves.

Operation of a rotameter under extreme sampling conditions, particularly extreme temperatures, complicates the calibration setup. It is difficult if not impossible for most laboratories to be able to calibrate flow metering devices at high temperatures or unusual gas mixtures (especially where toxic gases are involved). For these reasons, it is desirable to develop a calibration curve which is independent of the actual expected sampling conditions. As previously mentioned, the flow through a rotameter is dependent upon the value of C_m, the meter coefficient (see Equation A-7), which is a function of the Reynold's Number for the flow in the rotameter. Therefore, to be independent of the sampling conditions, the calibration curve must be in terms of C_m and N_{Re}.

Development of a Universal Calibration Curve

Solving Equation A-7 for C_m gives the following relationship:

(Eq. A-12)
$$C_m = \frac{Q_m D_f}{A_m}\left(\frac{P_m M_m}{g m_f R T_m}\right)^{1/2}$$

Dividing Equation A-11 by Equation A-12 yields:

$$\frac{N_{Re}}{C_m} = \frac{\dfrac{Q_m(D_t - D_f)P_m M_m}{A_m \mu_m R T_m}}{\dfrac{Q_m D_f}{A_m}\left(\dfrac{P_m M_m}{g m_f R T_m}\right)^{1/2}}$$

Cancelling the like terms Q_m and A_m yields:

$$\frac{N_{Re}}{C_m} = \frac{\dfrac{(D_t - D_f)P_m M_m}{\mu_m R T_m}}{D_f\left(\dfrac{P_m M_m}{g m_f R T_m}\right)^{1/2}}$$

Simplifying:

$$\frac{N_{Re}}{C_m} = \left[\frac{(D_t - D_f)P_m M_m}{\mu_m R T_m}\right]\left[\frac{1}{D_f}\left(\frac{g m_f R T_m}{P_m M_m}\right)^{1/2}\right]$$

Combining the like terms P_m, M_m, R and T_m yields:

(Eq. A-13)

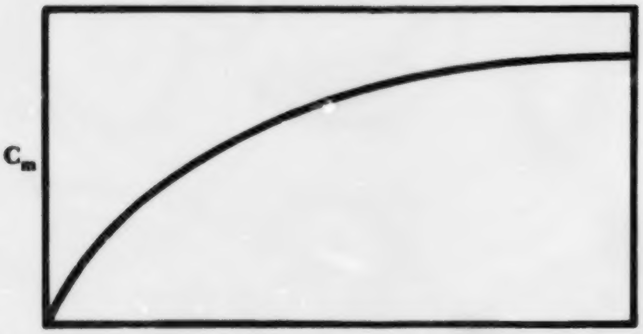
$$\frac{N_{Re}}{C_m} = \left[\frac{(D_t - D_f)}{\mu_m D_f}\right]\left(\frac{g m_f P_m M_m}{R T_m}\right)^{1/2}$$

Simplifying the $(D_t - D_f)$ and D_f relationship in Equation A-13 yields a dimensionless factor which has no limitations on either Reynold's Number or the meter coefficient C_m.

(Eq. A-14)

$$\frac{N_{Re}}{C_m} = \frac{1}{\mu_m}\left[\frac{D_t}{D_f} - 1\right]\left(\frac{g m_f P_m M_m}{R T_m}\right)^{1/2}$$

A plot of the dimensionless factor N_{Re}/C_m defined by Equation A-14 versus the meter coefficient C_m as calculated from Equation A-12 on regular graph paper will yield a universal calibration curve which is independent of the sampling conditions. Such a plot is illustrated in Figure A-7.



$$\frac{N_{Re}}{C_m} = \frac{1}{\mu m}\left[\left(\frac{D_t}{D_f}\right) - 1\right]\left(\frac{g m_f P_m M_m}{R T_m}\right)^{1/2}$$

Figure A-7. A universal calibration curve for a rotameter.

Use of the Universal Calibration Curve for a Rotameter

To Determine an Existing Flow Rate

To determine an existing flow rate, measurements must be made of the gas temperature and pressure as well as the float position. Data from the manufacturer of the rotameter will yield information on the diameter of the tube at the various float positions and on the diameter and mass of the float. The apparent molecular weight of the gas being metered can be calculated if the composition of the gas stream is known. The viscosity of the gas stream can be determined if the temperature of the gas stream is known (see Perry's Chemical Engineer's Handbook). From this data the N_{Re}/C_m factor (see Equation A-14) can be calculated. The universal calibration curve is then entered at the calculated value of N_{Re}/C_m and the corresponding C_m is noted. Q_m is then calculated from Equation A-7.

To Establish a Required Sampling Rate

To establish a required sampling rate, estimates are made of the metered gas pressure (P_m), the metered gas temperature (T_m), the apparent molecular weight of the metered gas (M_m), and the area of the meter (A_m) which will exist at the desired sampling rate. Using these estimated values, the meter coefficient C_m is calculated (see Equation A-12) for the desired sampling rate Q_m. The universal calibration curve (see Figure A-7) is entered at this value of C_m and the corresponding N_{Re}/C_m factor is noted. $[(D_t/D_f) - 1]$ is solved by using the following equation which is a rearrangement of Equation A-14:

(Eq. A-15)

$$\left[\left(\frac{D_t}{D_f}\right) - 1\right] = \mu_m \left(\frac{N_{Re}}{C_m}\right)\left(\frac{RT_m}{gm_fP_mM_m}\right)^{1/2}$$

The float position can be determined from the value $[(D_t/D_f) - 1]$. For some rotameters the value of $[(D_t/D_f) - 1]$ is the tube reading divided by 100. If the area of the meter corresponding to this float position is not equal to the original estimated value for the meter area, the new value of area is used as an estimate and the entire procedure is repeated until the estimated area and the calculated area are equal. Then upon setting the float position at this tube reading, T_m, P_m, and M_m are noted. If they are different from the original estimates, the procedure is repeated using the observed values of T_m, P_m, and M_m as estimates. Experience will aid in selecting original estimates that are nearly accurate so that the required sampling rate may be set fairly rapidly.

To Predict Calibration Curves

The above techniques are very cumbersome to apply in the field and as a result the universal calibration curve should not be used in such a manner.

The real utility of the universal calibration curve is that it can be used to predict calibration curves at any set of conditions. This results in a great reduction in laboratory work in that the rotameter need only be calibrated once and not every time the conditions at which the meter is operated change.

The first step in predicting calibration curves from the universal calibration curve of a rotameter is to ascertain the anticipated meter operating range for the sampling application of concern. Once this operating range is established, an arbitrary selection of a point on the universal calibration curve is made (see point in Figure A-8). The coordinates of point (a), N_{Re}/C_m (point b) and C_m (point c) are determined. Values of T_1, P_1, and M_1 and the value of N_{Re}/C_m are used to calculate a value for $D_t/D_f - 1$ by means of the following equation:

(Eq. A-15)

$$\left[\left(\frac{D_t}{D_f}\right) - 1\right] = \mu_m \left(\frac{N_{Re}}{C_m}\right)\left(\frac{RT_m}{gm_fP_mM_m}\right)^{1/2}$$

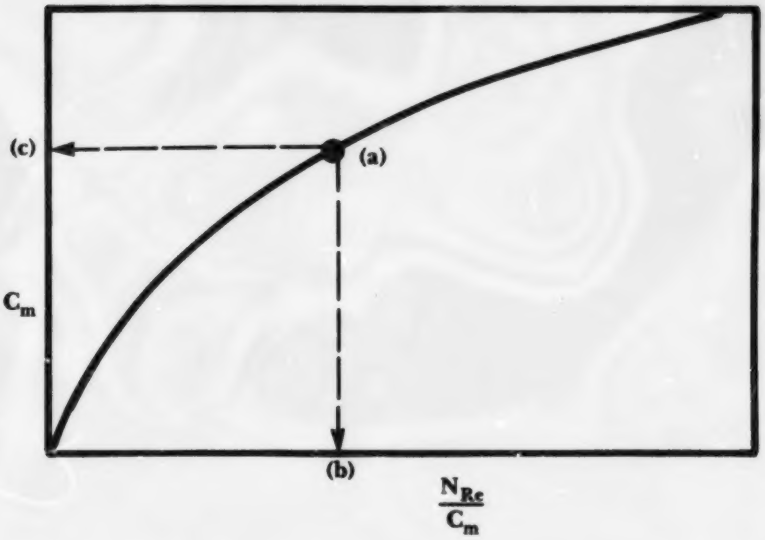


Figure A-8. Predicting calibration curves from the universal calibration curve.

The area of the meter (A_m) is calculated from this value of $[(D_t/D_f) - 1]$ and is used along with the assumed values of T_1, P_1, and M_1 and the value of C_m from the universal calibration curve to calculate a volumetric flow rate by means of the following equation:

(Eq. A-7)

$$Q_m = \left(\frac{C_mA_m}{D_f}\right)\left(\frac{gm_fRT_m}{P_mM_m}\right)^{1/2}$$

This procedure is repeated until enough points are available to plot a normal calibration curve. The entire procedure is repeated using new values for temperature, pressure, and molecular weight until a family of calibration curves is plotted. Of course this family of curves should bracket the anticipated meter operating conditions for the sampling application of concern. The volumetric flow rate (Q_m) is plotted versus either the area of the meter (A_m) or the tube reading which corresponds to the meter area.

Field operation is greatly simplified if the tube reading is used. A typical family of calibration curves is shown in Figure A-9.

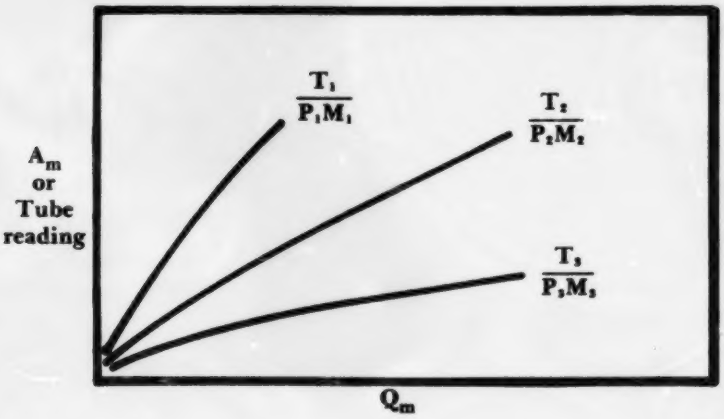


Figure A-9. Calibration curves predicted from universal calibration curve.

Notice that these curves are similar to the calibration curves illustrated in Figure A-6. The difference between them is the manner in which they were obtained. The curves of Figure A-6 were obtained by an actual laboratory calibration run for each set of conditions illustrated, whereas the curves of Figure A-9 were obtained by mathematical manipulation of data from only one calibration run. This can, of course, save considerable laboratory time. In addition, it may not be possible to ascertain, in the laboratory, calibration data at extreme conditions, particularly at high temperatures.

Appendix 2

Federal Register Reference Methods

Appendix A

APPENDIX A—REFERENCE METHOD FOR THE DETERMINATION OF SULFUR DIOXIDE IN THE ATMOSPHERE (PARAROSANILINE METHOD)

1. *Principle and Applicability.* 1.1 Sulfur dioxide is absorbed from air in a solution of potassium tetrachloromercurate (TCM). A dichlorosulfitomercurate complex, which resists oxidation by the oxygen in the air, is formed (*1, 2*). Once formed, this complex is stable to strong oxidants (e.g., ozone, oxides of nitrogen). The complex is reacted with pararosaniline and formaldehyde to form intensely colored pararosaniline methyl sulfonic acid (*3*). The absorbance of the solution is measured spectrophotometrically.

1.2 The method is applicable to the measurement of sulfur dioxide in ambient air using sampling periods up to 24 hours.

2. *Range and Sensitivity.* 2.1 Concentrations of sulfur dioxide in the range of 25 to 1,050 μg/m.^{3} (0.01 to 0.40 p.p.m.) can be measured under the conditions given. One can measure concentrations below 25 μg./m.^{3} by sampling larger volumes of air but only if the absorption efficiency of the particular system is first determined. Higher concentrations can be analyzed by using smaller gas samples, a larger collection volume, or a suitable aliquot of the collected sample. Beer's Law is followed through the working range from 0.03 to 1.0 absorbance units (0.8 to 27 μg. of sulfite ion in 25 ml. final solution computed as SO_2).

2.2 The lower limit of detection of sulfur dioxide in 10 ml. TCM is 0.75 μg. (based on twice the standard deviation) representing a concentration of 25 μg./m^3 SO_2 (0.01 p.p.m.) in an air sample of 30 liters.

3. *Interferences.* 3.1 The effects of the principal known interferences have been minimized or eliminated. Interferences by oxides of nitrogen are eliminated by sulfamic acid (*4, 5*), ozone by time-delay (*6*), and heavy metals by EDTA (ethylene-diamine-tetraacetic acid, disodium salt) and phosphoric acid (*4, 6*). At least 60 μg. Fe (III), 10 μg. Mn (II), and 10 μg. Cr (III) in 10 ml. absorbing reagent can be tolerated in the procedure. No significant interference was found with 10 μg. Cu (II) and 22 μg. V (V).

4. *Precision, Accuracy, and Stability.* 4.1 Relative standard deviation at the 95 percent confidence level is 4.6 percent for the analytical procedure using standard samples. (*5*)

4.2 After sample collection the solutions are relatively stable. At 22° C. losses of sulfur dioxide occur at the rate of 1 percent per day. When samples are stored at 5° C. for 30 days, no detectable losses of sulfur dioxide occur. The presence of EDTA enhances the stability of SO_2 in solution, and the rate of decay is independent of the concentration of SO_2. (*7*)

5. *Apparatus.*

5.1 *Sampling.*

5.1.1 *Absorber.* Absorbers normally used in air pollution sampling are acceptable for concentrations above 25 μg./m.^{3} (0.01 p.p.m.). An all-glass midget impinger, as shown in Figure A1, is recommended for 30-minute and 1-hour samples.

For 24-hour sampling, assemble an absorber from the following parts:

Polypropylene 2-port tube closures, special manufacture (available from Bel-Art Products, Pequannock, N.J.).

Glass impingers, 6 mm. tubing, 6 inches long, one end drawn to small diameter such that No. 79 jewelers drill will pass through, but No. 78 jewelers drill will not. (Other end fire polished.)

Polypropylene tubes, 164 by 32 mm. (Nalgene or equal).

5.1.2 *Pump.* Capable of maintaining an air pressure differential greater than 0.7 atmosphere at the desired flow rate.

5.1.3 *Air Flowmeter or Critical Orifice.* A calibrated rotameter or critical orifice capable of measuring air flow within ±2 percent. For 30-minute sampling, a 22-gauge hypodermic needle 1 inch long may be used as a critical orifice to give a flow of about 1 liter/minute. For 1-hour sampling, a 23-gauge hypodermic needle five-eighths of an inch long may be used as a critical orifice to give a flow of about 0.5 liter/minute. For 24-hour sampling, a 27-gauge hypodermic needle three-eighths of an inch long may be used to give a flow of about 0.2 liter/minute. Use a membrane filter to protect the needle (Figure A1a).

5.2 *Analysis.*

5.2.1 *Spectrophotometer.* Suitable for measurement of absorbance at 548 nm. with an effective spectral band width of less than 15 nm. Reagent blank problems may occur with spectrophotometers having greater spectral band width. The wavelength calibration of the instrument should be verified. If transmittance is measured, this can be converted to absorbance:

$$A = \log_{10}(1/T)$$

6. *Reagents.*

6.1 *Sampling.*

6.1.1 *Distilled water.* Must be free from oxidants.

6.1.2 *Absorbing Reagent [0.04 M Potassium Tetrachloromercurate (TCM)].* Dissolve 10.86 g. mercuric chloride, 0.066 g. EDTA (ethylenediaminetetraacetic acid, disodium salt), and 6.0 g. potassium chloride in water and bring to mark in a 1,000-ml. volumetric flask. (Caution: Highly poisonous. If spilled on skin, flush off with water immediately). The pH of this reagent should be approximately 4.0, but it has been shown that there is no appreciable difference in collection efficiency over the range of pH 5 to pH 3.(*7*). The absorbing reagent is normally stable for 6 months. If a precipitate forms, discard the reagent.

6.2 *Analysis.*

6.2.1 *Sulfamic Acid (0.6 percent).* Dissolve 0.6 g. sulfamic acid in 100 ml. distilled water. Prepare fresh daily.

6.2.2 *Formaldehyde (0.2 percent).* Dilute 5 ml. formaldehyde solution (36-38 percent) to 1,000 ml. with distilled water. Prepare daily.

6.2.3 *Stock Iodine Solution (0.1 N).* Place 12.7 g. iodine in a 250-ml. beaker; add 40 g. potassium iodide and 25 ml. water. Stir until all is dissolved, then dilute to 1,000 ml. with distilled water.

6.2.4 *Iodine Solution (0.01 N).* Prepare approximately 0.01 N iodine solution by diluting 50 ml. of stock solution to 500 ml. with distilled water.

6.2.5 *Starch Indicator Solution.* Triturate 0.4 g. soluble starch and 0.002 g. mercuric iodide (preservative) with a little water, and add the paste slowly to 200 ml. boiling water. Continue boiling until the solution is clear; cool, and transfer to a glass-stoppered bottle.

6.2.6 *Stock Sodium Thiosulfate Solution (0.1 N).* Prepare a stock solution by dissolving 25 g. sodium thiosulfate ($Na_2S_2O_3 \cdot 5H_2O$) in 1,000 ml freshly boiled, cooled, distilled water and add 0.1 g. sodium carbonate to the solution. Allow the solution to stand 1 day before standardizing. To standardize, accurately weigh, to the nearest 0.1 mg., 1.5 g. primary standard potassium iodate dried at 180° C. and dilute to volume in a 500-ml. volumetric flask. To a 500-ml. iodine flask, pipet 50 ml. of iodate solution. Add 2 g. potassium iodide and 10 ml. of 1 N hydrochloric acid. Stopper the flask. After 5 minutes, titrate with stock thiosulfate solution to a pale yellow. Add 5 ml. starch indicator solution and continue the titration until the blue color disappears. Calculate the normality of the stock solution:

$$N = (W/M) \times 2.80$$

N = Normality of stock thiosulfate solution.
M = Volume of thiosulfate required, ml.
W = Weight of potassium iodate, grams.

$2.80 = [10^3$ (conversion of g. to mg.) $\times$ 0.1 (fraction iodate used)]/35.67 (equivalent weight of potassium iodate)

6.2.7 *Sodium Thiosulfate Titrant (0.01 N).* Dilute 100 ml. of the stock thiosulfate solution to 1,000 ml. with freshly boiled distilled water.

$$\text{Normality} = \text{Normality of stock solution} \times 0.100.$$

6.2.8 *Standardized Sulfite Solution for Preparation of Working Sulfite-TCM Solution.* Dissolve 0.3 g. sodium metabisulfite ($Na_2S_2O_5$) or 0.40 g. sodium sulfite (Na_2SO_3) in 500 ml. of recently boiled, cooled, distilled water. (Sulfite solution is unstable; it is therefore important to use water of the highest purity to minimize this instability.) This solution contains the equivalent of 320 to 400 μg./ml. of SO_2. The actual concentration of the solution is determined by adding excess iodine and back-titrating with standard sodium thiosulfate solution. To back-titrate, pipet 50 ml. of the 0.01 N iodine into each of two 500-ml. iodine flasks (A and B). To flask A (blank) add 25 ml. distilled water, and to flask B (sample) pipet 25 ml. sulfite solution. Stopper the flasks and allow to react for 5 minutes. Prepare the working sulfite-TCM Solution (6.2.9) at the same time iodine solution is added to the flasks. By means of a buret containing standardized 0.01 N thiosulfate, titrate each flask in turn to a pale yellow. Then add 5 ml. starch solution and continue the titration until the blue color disappears.

6.2.9 *Working Sulfite-TCM Solution.* Pipet accurately 2 ml. of the standard solution into a 100 ml volumetric flask and bring to mark with 0.04 M TCM. Calculate the concentration of sulfur dioxide in the working solution:

$$\mu g\, SO_2/\text{ml.} = ((A - B)(N)(32{,}000)/25)(\times 0.02)$$

A = Volume thiosulfate for blank, ml.
B = Volume thiosulfate for sample, ml.
N = Normality of thiosulfate titrant.
32,000 = Milliequivalent wt. of SO_2, μg.
25 = Volume standard sulfite solution, ml.
0.02 = Dilution factor.

This solution is stable for 30 days if kept at 5° C. (refrigerator). If not kept at 5° C., prepare daily.

6.2.10 *Purified Pararosaniline Stock Solution (0.2 percent nominal).*

6.2.10.1 *Dye Specifications.* The pararosaniline dye must meet the following performance specifications: (1) The dye must have a wavelength of maximum absorbance at 540 nm. when assayed in a buffered solution of 0 1 M sodium acetate-acetic acid; (2) the absorbance of the reagent blank, which is temperature-sensitive (0.015 absorbance unit/°C), should not exceed 0.170 absorbance unit at 22° C. with a 1-cm. optical path length, when the blank is prepared according to the prescribed analytical procedure and to the specified concentration of the dye; (3) the calibration curve (Section 8.2.1) should have a slope of 0.030±0.002 absorbance units/µg. SO_2 at this path length when the dye is pure and the sulfite solution is properly standardized.

6.2.10.2 *Preparation of Stock Solution.* A specially purified (99-100 percent pure) solution of pararosaniline, which meets the above specifications, is commercially available in the required 0.20 percent concentration (Harleco*). Alternatively, the dye may be purified, a stock solution prepared and then assayed according to the procedure of Scaringelli, et al. (*4*)

6.2.11 *Pararosaniline Reagent.* To a 250-ml. volumetric flask, add 20 ml. stock pararosaniline solution. Add an additional 0.2 ml. stock solution for each percent the stock assays below 100 percent. Then add 25 ml. 3 M phosphoric acid and dilute to volume with distilled water. This reagent is stable for at least 9 months.

7. *Procedure.*

7.1 *Sampling.* Procedures are described for short-term (30 minutes and 1 hour) and for long-term (24 hours) sampling. One can select different combinations of sampling rate and time to meet special needs. Sample volumes should be adjusted, so that linearity is maintained between absorbance and concentration over the dynamic range.

7.1.1 *30-Minute and 1-Hour Samplings.* Insert a midget impinger into the sampling system, Figure A1. Add 10 ml. TCM solution to the impinger. Collect sample at 1 liter/minute for 30 minutes, or at 0.5 liter/minute for 1 hour, using either a rotameter, as shown in Figure A1, or a critical orifice, as shown in Figure A1a, to control flow. Shield the absorbing reagent from direct sunlight during and after sampling by covering the impinger with aluminum foil, to prevent deterioration. Determine the volume of air sampled by multiplying the flow rate by the time in minutes and record the atmospheric pressure and temperature. Remove and stopper the impinger. If the sample must be stored for more than a day before analysis, keep it at 5° C. in a refrigerator (see 4.2).

7.1.2 *24-Hour Sampling.* Place 50 ml. TCM solution in a large absorber and collect the sample at 0.2 liter/minute for 24 hours from midnight to midnight. Make sure no entrainment of solution results with the impinger. During collection and storage protect from direct sunlight. Determine the total air volume by multiplying the air flow rate by the time in minutes. The correction of 24-hour measurements for temperature and pressure is extremely difficult and is not ordinarily done. However, the accuracy of the measurement will be improved if meaningful corrections can be applied. If storage is necessary, refrigerate at 5° C. (see 4.2).

7.2 *Analysis.*

7.2.1 *Sample Preparation.* After collection, if a precipitate is observed in the sample, remove it by centrifugation.

7.2.1.1 *30-Minute and 1-Hour Samples.* Transfer the sample quantitatively to a 25-ml. volumetric flask; use about 5 ml. distilled water for rinsing. Delay analyses for 20 minutes to allow any ozone to decompose.

7.2.1.2 *24-Hour Sample.* Dilute the entire sample to 50 ml. with absorbing solution. Pipet 5 ml. of the sample into a 25-ml. volumetric flask for chemical analyses. Bring volume to 10 ml. with absorbing reagent. Delay analyses for 20 minutes to allow any ozone to decompose.

7.2.2 *Determination.* For each set of determinations prepare a reagent blank by adding 10 ml. unexposed TCM solution to a 25-ml. volumetric flask. Prepare a control solution by adding 2 ml. of working sulfite-TCM solution and 8 ml. TCM solution to a 25-ml. volumetric flask. To each flask containing either sample, control solution, or reagent blank, add 1 ml. 0.6 percent sulfamic acid and allow to react 10 minutes to destroy the nitrite from oxides of nitrogen. Accurately pipet in 2 ml. 0.2 percent formaldehyde solution, then 5 ml. pararosaniline solution. Start a laboratory timer that has been set for 30 minutes. Bring all flasks to volume with freshly boiled and cooled distilled water and mix thoroughly. After 30 minutes and before 60 minutes, determine the absorbances of the sample (denote as A), reagent blank (denote as A_o) and the control solution at 548 nm. using 1-cm. optical path length cells. Use distilled water, not the reagent blank, as the reference. (NOTE! This is important because of the color sensitivity of the reagent blank to temperature changes which can be induced in the cell compartment of a spectrophotometer.) Do not allow the colored solution to stand in the absorbance cells, because a film of dye may be deposited. Clean cells with alcohol after use. If the temperature of the determinations does not differ by more than 2° C. from the calibration temperature (8.2), the reagent blank should be within 0.03 absorbance unit of the y-intercept of the calibration curve (8.2). If the reagent blank differs by more than 0.03 absorbance unit from that found in the calibration curve, prepare a new curve.

7.2.3 *Absorbance Range.* If the absorbance of the sample solution ranges between 1.0 and 2.0, the sample can be diluted 1:1 with a portion of the reagent blank and read within a few minutes. Solutions with higher absorbance can be diluted up to sixfold with the reagent blank in order to obtain onscale readings within 10 percent of the true absorbance value.

8. *Calibration and Efficiencies.*

8.1 *Flowmeters and Hypodermic Needle.* Calibrate flowmeters and hypodermic needle (*8*) against a calibrated wet test meter.

8.2 *Calibration Curves.*

8.2.1 *Procedure with Sulfite Solution.* Accurately pipet graduated amounts of the working sulfite-TCM solution (6.2.9) (such as 0, 0.5, 1, 2, 3, and 4 ml.) into a series of 25-ml. volumetric flasks. Add sufficient TCM solution to each flask to bring the volume to approximately 10 ml. Then add the remaining reagents as described in 7.2.2. For maximum precision use a constant-temperature bath. The temperature of calibration must be maintained within ±1° C. and in the range of 20° to 30° C. The temperature of calibration and the temperature of analysis must be within 2 degrees. Plot the absorbance against the total concentration in µg. SO_2 for the corresponding solution. The total µg. SO_2 in solution equals the concentration of the standard (Section 6.2.9) in µg. SO_2/ml. times the ml. sulfite solution added (µg. SO_2 = µg./l. SO_2 × ml. added). A linear relationship should be obtained, and the y-intercept should be within 0.03 absorbance unit of the zero standard absorbance. For maximum precision determine the line of best fit using regression analysis by the method of least squares. Determine the slope of the line of best fit, calculate its reciprocal and denote as B_s. B_s is the calibration factor. (See Section 6.2.10.1 for specifications on the slope of the calibration curve). This calibration factor can be used for calculating results provided there are no radical changes in temperature or pH. At least one control sample containing a known concentration of SO_2 for each series of determinations, is recommended to insure the reliability of this factor.

8.2.2 *Procedure with SO_2 Permeation Tubes.*

8.2.2.1 *General Considerations.* Atmospheres containing accurately known amounts of sulfur dioxide at levels of interest can be prepared using permeation tubes. In the systems for generating these atmospheres, the permeation tube emits SO_2 gas at a known, low, constant rate, provided the temperature of the tube is held constant (±0.1° C.) and provided the tube has been accurately calibrated at the temperature of use. The SO_2 gas permeating from the tube is carried by a low flow of inert gas to a mixing chamber where it is accurately diluted with SO_2-free air to the level of interest and the sample taken. These systems are shown schematically in Figures A2 and A3 and have been described in detail by O'Keeffe and Ortman (*9*), Scaringelli, Frey, and Saltzman (*10*), and Scaringelli, O'Keeffe, Rosenberg, and Bell (*11*).

8.2.2.2 *Preparation of Standard Atmospheres.* Permeation tubes may be prepared or purchased. Scaringelli, O'Keeffe, Rosenberg, and Bell (*11*) give detailed, explicit directions for permeation tube calibration. Tubes with a certified permeation rate are available from the National Bureau of Standards. Tube permeation rates from 0.2 to 0.4 µg./minute, inert gas flows of about 50 ml./minute, and dilution air flow rates from 1.1 to 15 liters/minute conveniently give standard atmospheres containing desired levels of SO_2 (25 to 390 µg./m.³; 0.01 to 0.15 p.p.m. SO_2). The concentration of SO_2 in any standard atmosphere can be calculated as follows:

$$C=(P\times 10^{3})/(R_d+R_i)$$

---

*Hartmen-Leddon, 60th and Woodland Avenue, Philadelphia, PA 19143.

Where:

C = Concentration of SO_2, μg./m.³ at reference conditions.

P = Tube permeation rate, μg./minute.

R_d = Flow rate of dilution air, liter/minute at reference conditions.

R_i = Flow rate of inert gas, liter/minute at reference conditions.

8.2.2.3 *Sampling and Preparation of Calibration Curve.* Prepare a series (usually six) of standard atmospheres containing SO_2 levels from 25 to 390 μg. SO_2/m.³. Sample each atmosphere using similar apparatus and taking exactly the same air volume as will be done in atmospheric sampling. Determine absorbances as directed in 7.2. Plot the concentration of SO_2 in μg./m.³ (x-axis) against $A-A_0$ values (y-axis) draw the straight line of best fit and determine the slope. Alternatively, regression analysis by the method of least squares may be used to calculate the slope. Calculate the reciprocal of the slope and denote as B_g.

8.3 *Sampling Efficiency.* Collection efficiency is above 98 percent; efficiency may fall off, however, at concentrations below 25 μg./m.³. *(12, 13)*

9. *Calculations.*

9.1 *Conversion of Volume.* Convert the volume of air sampled to the volume at reference conditions of 25° C. and 760 mm. Hg. (On 24-hour samples, this may not be possible.)

$$V_R = V \times (P/760) \times (298/t+273)$$

V_R = Volume of air at 25° C. and 760 mm. Hg, liters.

V = Volume of air sampled, liters.

P = Barometric pressure, mm. Hg.

t = Temperature of air sample, °C.

9.2 *Sulfur Dioxide Concentration.*

9.2.1 When sulfite solutions are used to prepare calibration curves, compute the concentration of sulfur dioxide in the sample:

$$\mu g.\ SO_2/m.^3 = [((A-A_0)(10^3)(B_s))/V_R] \times D$$

A = Sample absorbance.

A_0 = Reagent blank absorbance.

10^3 = Conversion of liters to cubic meters.

V_R = The sample corrected to 25° C. and 760 mm. Hg, liters.

B_s = Calibration factor, μg./absorbance unit.

D = Dilution factor. For 30-minute and 1-hour samples, $D = 1$. For 24-hour samples, $D = 10$.

9.2.2 When SO_2 gas standard atmospheres are used to prepare calibration curves, compute the sulfur dioxide in the sample by the following formula:

$$SO_2,\ \mu g./m.^3 = (A-A_0) \times B_g$$

A = Sample absorbance.

A_0 = Reagent blank absorbance.

B_g = (See 8.2.2.3).

9.2.3 *Conversion of μg./m.³ to p.p.m.* = If desired, the concentration of sulfur dioxide may be calculated as p.p.m. SO_2 at reference conditions as follows:

$$p.p.m.\ SO_2 = \mu g.\ SO_2/m.^3 \times 3.82 \times 10^{-4}$$

10. *References.*

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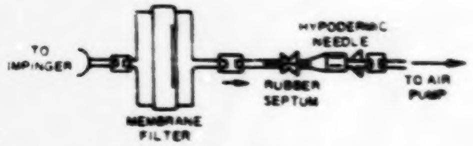

Figure A1a. Critical orifice flow control.

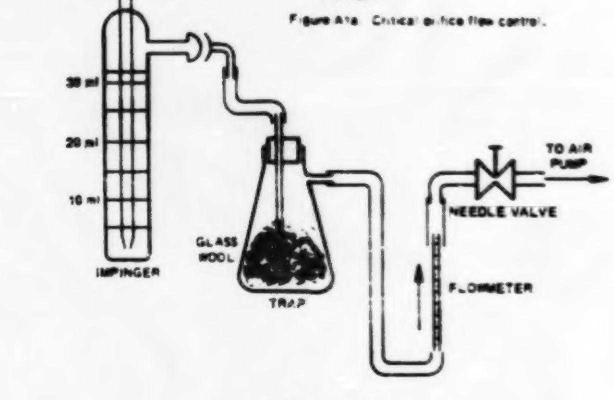

Figure A1. Sampling train.

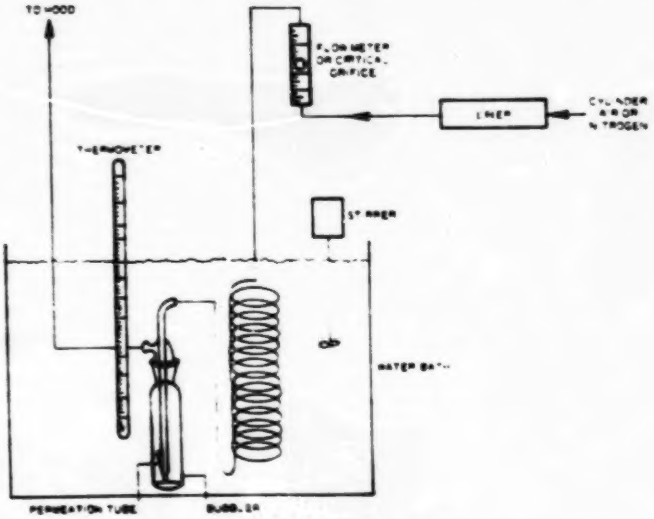
TO HOOD
FLOW METER
OR CRITICAL
ORIFICE
DRIER
CYLINDER
AIR OR
NITROGEN
THERMOMETER
STIRRER
WATER BATH
PERMEATION TUBE
BUBBLER

Figure A2. Apparatus for gravimetric calibration and field use.

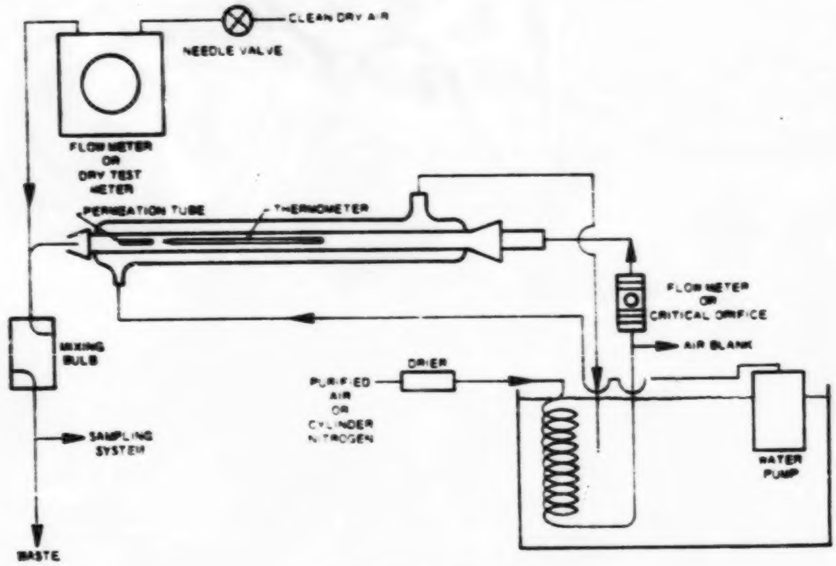
CLEAN DRY AIR
NEEDLE VALVE
FLOW METER
OR
DRY TEST
METER
PERMEATION TUBE
THERMOMETER
FLOW METER
OR
CRITICAL ORIFICE
AIR BLANK
MIXING
BULB
DRIER
PURIFIED
AIR
OR
CYLINDER
NITROGEN
SAMPLING
SYSTEM
WATER
PUMP
WASTE

Figure A3. Permeation tube schematic for laboratory use.

Appendix B

APPENDIX B—REFERENCE METHOD FOR THE DETERMINATION OF SUSPENDED PARTICULATES IN THE ATMOSPHERE (HIGH VOLUME METHOD)

1. *Principle and Applicability.*

1.1 Air is drawn into a covered housing and through a filter by means of a high-flow-rate blower at a flow rate (1.13 to 1.70 m.^{3}/min.; 40 to 60 ft.^{3}/min.) that allows suspended particles having diameters of less than 100 µm. (Stokes equivalent diameter) to pass to the filter surface. (*1*) Particles within the size range of 100 to 0.1µm. diameter are ordinarily collected on glass fiber filters. The mass concentration of suspended particulates in the ambient air (µg./m.^{3}) is computed by measuring the mass of collected particulates and the volume of air sampled.

1.2 This method is applicable to measurement of the mass concentration of suspended particulates in ambient air. The size of the sample collected is usually adequate for other analyses.

2. *Range and Sensitivity.*

2.1 When the sampler is operated at an average flow rate of 1.70 m.^{3}/min. (60 ft.^{3}/min.) for 24 hours, an adequate sample will be obtained even in an atmosphere having concentrations of suspended particulates as low as 1 µg./m.^{3}. If particulate levels are unusually high, a satisfactory sample may be obtained in 6 to 8 hours or less. For determination of average concentrations of suspended particulates in ambient air, a standard sampling period of 24 hours is recommended.

2.2 Weights are determined to the nearest milligram, airflow rates are determined to the nearest 0.03 m.^{3}/min. (1.0 ft.^{3}/min.), times are determined to the nearest 2 minutes, and mass concentrations are reported to the nearest microgram per cubic meter.

3. *Interferences.*

3.1 Particulate matter that is oily, such as photochemical smog or wood smoke, may block the filter and cause a rapid drop in airflow at a nonuniform rate. Dense fog or high humidity can cause the filter to become too wet and severely reduce the airflow through the filter.

3.2 Glass-fiber filters are comparatively insensitive to changes in relative humidity, but collected particulates can be hygroscopic. (*2*)

4. *Precision, Accuracy, and Stability.*

4.1 Based upon collaborative testing, the relative standard deviation (coefficient of variation) for single analyst variation (repeatability of the method) is 3.0 percent. The corresponding value for multilaboratory variation (reproducibility of the method) is 3.7 percent. (*3*)

4.2 The accuracy with which the sampler measures the true average concentration depends upon the constancy of the airflow rate through the sampler. The airflow rate is affected by the concentration and the nature of the dust in the atmosphere. Under these conditions the error in the measured average concentration may be in excess of ±50 percent of the true average concentration, depending on the amount of reduction of airflow rate and on the variation of the mass concentration of dust with time during the 24-hour sampling period. (*4*)

5. *Apparatus.*

5.1 *Sampling.*

5.1.1 *Sampler.* The sampler consists of three units: (1) The faceplate and gasket, (2) the filter adapter assembly, and (3) the motor unit. Figure B1 shows an exploded view of these parts, their relationship to each other, and how they are assembled. The sampler must be capable of passing environmental air through a 406.5 cm.^{2} (63 in.^{2}) portion of a clean 20.3 by 25.4 cm. (8- by 10-in.) glass-fiber filter at a rate of at least 1.70 m.^{3}/min. (60 ft.^{3}/min.). The motor must be capable of continuous operation for 24-hour periods with input voltages ranging from 110 to 120 volts, 50–60 cycles alternating current and must have third-wire safety ground. The housing for the motor unit may be of any convenient construction so long as the unit remains airtight and leak-free. The life of the sampler motor can be extended by lowering the voltage by about 10 percent with a small "buck or boost" transformer between the sampler and power outlet.

5.1.2 *Sampler Shelter.* It is important that the sampler be properly installed in a suitable shelter. The shelter is subjected to extremes of temperature, humidity, and all types of air pollutants. For these reasons the materials of the shelter must be chosen carefully. Properly painted exterior plywood or heavy gauge aluminum serve well. The sampler must be mounted vertically in the shelter so that the glass-fiber filter is parallel with the ground. The shelter must be provided with a roof so that the filter is protected from precipitation and debris. The internal arrangement and configuration of a suitable shelter with a gable roof are shown in Figure B2. The clearance area between the main housing and the roof at its closest point should be 580.5±193.5 cm.^{2} (90±30 in.^{2}).The main housing should be rectangular, with dimensions of about 29 by 36 cm. (11½ by 14 in.).

5.1.3 *Rotameter.* Marked in arbitrary units, frequently 0 to 70, and capable of being calibrated. Other devices of at least comparable accuracy may be used.

5.1.4 *Orifice Calibration Unit.* Consisting of a metal tube 7.6 cm. (3 in.) ID and 15.9 cm. (6¼ in.) long with a static pressure tap 5.1 cm. (2 in.) from one end. See Figure B3. The tube end nearest the pressure tap is flanged to about 10.8 cm. (4¼ in.) OD with a male thread of the same size as the inlet end of the high-volume air sampler. A single metal plate 9.2 cm. (3⅝ in.) in diameter and 0.24 cm. ($\frac{3}{32}$ in.) thick with a central orifice 2.9 cm. (1⅛ in.) in diameter is held in place at the air inlet end with a female threaded ring. The other end of the tube is flanged to hold a loose female threaded coupling, which screws onto the inlet of the sampler. An 18-hole metal plate, an integral part of the unit, is positioned between the orifice and sampler to simulate the resistance of a clean glass-fiber filter. An orifice calibration unit is shown in Figure B3.

5.1.5 *Differential Manometer.* Capable of measuring to at least 40 cm. (16 in.) of water.

5.1.6 *Positive Displacement Meter.* Calibrated in cubic meters or cubic feet, to be used as a primary standard.

5.1.7 *Barometer.* Capable of measuring atmospheric pressure to the nearest mm.

5.2 *Analysis.*

5.2.1 *Filter Conditioning Environment.* Balance room or desiccator maintained at 15° to 35° C. and less than 50 percent relative humidity.

5.2.2 *Analytical Balance.* Equipped with a weighing chamber designed to handle unfolded 20.3 by 25.4 cm. (8- by 10-in.) filters and having a sensitivity of 0.1 mg.

5.2.3 *Light Source.* Frequently a table of the type used to view X-ray films.

5.2.4 *Numbering Device.* Capable of printing identification numbers on the filters.

6. *Reagents.*

6.1 *Filter Media.* Glass-fiber filters having a collection efficiency of at least 99 percent for particles of 0.3 µm. diameter, as measured by the DOP test, are suitable for the quantitative measurement of concentrations of suspended particulates, (*5*) although some other medium, such as paper, may be desirable for some analyses. If a more detailed analysis is contemplated, care must be exercised to use filters that contain low background concentrations of the pollutant being investigated. Careful quality control is required to determine background values of these pollutants.

7. *Procedure.*

7.1 *Sampling.*

7.1.1 *Filter Preparation.* Expose each filter to the light source and inspect for pinholes, particles, or other imperfections. Filters with visible imperfections should not be used. A small brush is useful for removing particles. Equilibrate the filters in the filter conditioning environment for 24 hours. Weigh the filters to the nearest milligram; record tare weight and filter identification number. Do not bend or fold the filter before collection of the sample.

7.1.2 *Sample Collection.* Open the shelter, loosen the wing nuts, and remove the faceplate from the filter holder. Install a numbered, preweighed, glass-fiber filter in position (rough side up), replace the faceplate without disturbing the filter, and fasten securely. Undertightening will allow air leakage, overtightening will damage the sponge-rubber faceplate gasket. A very light application of talcum powder may be used on the sponge-rubber faceplate gasket to prevent the filter from sticking. During inclement weather the sampler may be removed to a protected area for filter change. Close the roof of the shelter, run the sampler for about 5 minutes, connect the rotameter to the nipple on the back of the sampler, and read the rotameter ball with rotameter in a vertical position. Estimate to the nearest whole number. If the ball is fluctuating rapidly, tip the rotameter and slowly straighten it until the ball gives a constant reading. Disconnect the rotameter from the nipple; record the initial rotameter reading and the starting time and date on the filter folder. (The rotameter should never be connected to the sampler except when the flow is being measured.) Sample for 24 hours from midnight to midnight and take a final rotameter reading. Record the final rotameter reading and ending time and date on the filter folder. Remove the faceplate as described above and carefully remove the filter from the holder, touching only the outer edges. Fold the filter lengthwise so that only surfaces with collected particulates are in contact, and place in a manila folder. Record on the folder the filter number, location, and any other factors, such as meteorological conditions or razing of nearby buildings, that might affect the results. If the sample is defective, void it at this time. In order to obtain a valid sample, the high-volume sampler must be operated with the same rotameter and tubing that were used during its calibration.

7.2 *Analysis.* Equilibrate the exposed filters for 24 hours in the filter conditioning environment, then reweigh. After they are weighed, the filters may be saved for detailed chemical analysis.

7.3 *Maintenance.*

7.3.1 *Sampler Motor.* Replace brushes before they are worn to the point where motor damage can occur.

7.3.2 *Faceplate Gasket.* Replace when the margins of samples are no longer sharp. The gasket may be sealed to the faceplate with rubber cement or double-sided adhesive tape.

7.3.3 *Rotameter.* Clean as required, using alcohol.

8. *Calibration.*

8.1 *Purpose.* Since only a small portion of the total air sampled passes through the rotameter during measurement, the rotameter must be calibrated against actual airflow with the orifice calibration unit. Before the orifice calibration unit can be used to calibrate the rotameter, the orifice calibration unit itself must be calibrated against the positive displacement primary standard.

8.1.1 *Orifice Calibration Unit.* Attach the orifice calibration unit to the intake end of the positive displacement primary standard and attach a high-volume motor blower unit to the exhaust end of the primary standard. Connect one end of a differential manometer to the differential pressure tap of the orifice calibration unit and leave the other end open to the atmosphere. Operate the high-volume motor blower unit so that a series of different, but constant, airflows (usually six) are obtained for definite time periods. Record the reading on the differential manometer at each airflow. The different constant airflows are obtained by placing a series of loadplates, one at a time, between the calibration unit and the primary standard. Placing the orifice before the inlet reduces the pressure at the inlet of the primary standard below atmospheric; therefore, a correction must be made for the increase in volume caused by this decreased inlet pressure. Attach one end of a second differential manometer to an inlet pressure tap of the primary standard and leave the other open to the atmosphere. During each of the constant airflow measurements made above, measure the true inlet pressure of the primary standard with this second differential manometer. Measure atmospheric pressure and temperature. Correct the measured air volume to true air volume as directed in 9.1.1, then obtain true airflow rate, Q, as directed in 9.1.3. Plot the differential manometer readings of the orifice unit versus Q.

8.1.2 *High-Volume Sampler.* Assemble a high-volume sampler with a clean filter in place and run for at least 5 minutes. Attach a rotameter, read the ball, adjust so that the ball reads 65, and seal the adjusting mechanism so that it cannot be changed easily. Shut off motor, remove the filter, and attach the orifice calibration unit in its place. Operate the high-volume sampler at a series of different, but constant, airflows (usually six). Record the reading of the differential manometer on the orifice calibration unit, and record the readings of the rotameter at each flow. Measure atmospheric pressure and temperature. Convert the differential manometer reading to m.^{3}/min., Q, then plot rotameter reading versus Q.

8.1.3 *Correction for Differ[illegible]s in Pressure or Temperature.* See Ad[illegible]m B.

9. *Calculations.*

9.1 *Calibration of Orifice.*

9.1.1 *True Air Volume.* Calculate the air volume measured by the positive displacement primary standard.

$$V_a = ((P_a - P_m)/P_a)(V_M)$$

V_a = True air volume at atmospheric pressure, m.^{3}

P_a = Barometric pressure, mm. Hg.

P_m = Pressure drop at inlet of primary standard, mm. Hg.

V_M = Volume measured by primary standard, m.^{3}

9.1.2 *Conversion Factors.*

Inches Hg. × 25.4 = mm. Hg.
Inches water × 73.48 × 10^{-3} = inches Hg.
Cubic feet air × 0.0284 = cubic meters air.

9.1.3 *True Airflow Rate.*

$$Q = V_a/T$$

Q = Flow rate, m.^{3}/min.

T = Time of flow, min.

9.2 *Sample Volume.*

9.2.1 *Volume Conversion.* Convert the initial and final rotameter readings to true airflow rate, Q, using calibration curve of 8.1.2.

9.2.2 *Calculate volume of air sampled*

$$V = (Q_iQ_f/2) \times T$$

V = Air volume sampled, m.^{3}

Q_i = Initial airflow rate, m.^{3}/min.

Q_f = Final airflow rate, m.^{3}/min.

T = Sampling time, min.

9.3 *Calculate mass concentration of suspended particulates*

$$S.P. = [(W_f - W_i) \times 10^6]/V$$

S.P. = Mass concentration of suspended particulates, µg/m.^{3}

W_i = Initial weight of filter, g.

W_f = Final weight of filter, g.

V = Air volume sampled, m.^{3}

10^6 = Conversion of g. to µg.

10. *References.*

(*1*) Robson, C. D., and Foster, K. E., "Evaluation of Air Particulate Sampling Equipment", *Am. Ind. Hyg. Assoc. J. 24*, 404 (1962).

(*2*) Tierney, G. P., and Conner, W. D., "Hygroscopic Effects on Weight Determinations of Particulates Collected on Glass-Fiber Filters", *Am. Ind. Hyg. Assoc. J. 28*, 363 (1967).

(*3*) Unpublished data based on a collaborative test involving 12 participants, conducted under the direction of the Methods Standardization Services Section of the National Air Pollution Control Administration, October, 1970.

(*4*) Harrison, W. K., Nader, J. S., and Fugman, F. S., "Constant Flow Regulators for High-Volume Air Sampler", *Am. Ind. Hyg. Assoc. J. 21*, 114-120 (1960).

(*5*) Pate, J. B., and Tabor, E. C., "Analytical Aspects of the Use of Glass-Fiber Filters for the Collection and Analysis of Atmospheric Particulate Matter", *Am. Ind. Hyg. Assoc. J. 23*, 144-150 (1962).

ADDENDA

A. *Alternative Equipment.*

A modification of the high-volume sampler incorporating a method for recording the actual airflow over the entire sampling period has been described, and is acceptable for measuring the concentration of suspended particulates (Henderson, J. S., Eighth Conference on Methods in Air Pollution and Industrial Hygiene Studies, 1967, Oakland, Calif.). This modification consists of an exhaust orifice meter assembly connected through a transducer to a system for continuously recording airflow on a circular chart. The volume of air sampled is calculated by the following equation:

$$V = Q \times T$$

Q = Average sampling rate, m.^{3}/min.

T = Sampling time, minutes.

The average sampling rate, Q, is determined from the recorder chart by estimation if the flow rate does not vary more than 0.11 m.^{3}/min. (4 ft.^{3}/min.) during the sampling period. If the flow rate does vary more than 0.11 m.^{3} (4 ft.^{3}/min.) during the sampling period, read the flow rate from the chart at 2-hour intervals and take the average.

B. *Pressure and Temperature Corrections.*

If the pressure or temperature during high-volume sampler calibration is substantially different from the pressure or temperature during orifice calibration, a correction of the flow rate, Q, may be required. If the pressures differ by no more than 15 percent and the temperatures differ by no more than 100 percent (°C), the error in the uncorrected flow rate will be no more than 15 percent. If necessary, obtain the corrected flow rate as directed below. This correction applies only to orifice meters having a constant orifice coefficient. The coefficient for the calibrating orifice described in 5.1.4 has been shown experimentally to be constant over the normal operating range of the high-volume sampler (0.6 to 2.2 m.^{3}/min.; 20 to 78 ft.^{3}/min.). Calculate corrected flow rate:

$$Q_2 = Q_1[T_2P_1/T_1P_2]^{1/2}$$

Q_2 = Corrected flow rate, m.^{3}/min.

Q_1 = Flow rate during high-volume sampler calibration (Section 8.1.2), m.^{3}/min.

T_1 = Absolute temperature during orifice unit calibration (Section 8.1.1), °K or °R.

P_1 = Barometric pressure during orifice unit calibration (Section 8.1.1), mm. Hg.

T_2 = Absolute temperature during high-volume sampler calibration (Section 8.1.2), °K or °R.

P_2 = Barometric pressure during high-volume sampler calibration (Section 8.1.2), mm. Hg.

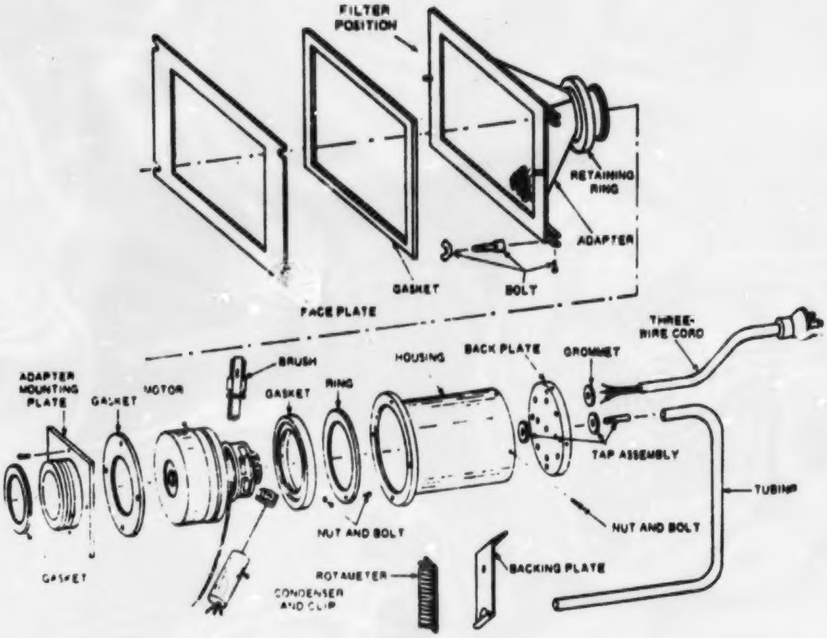
FILTER POSITION
RETAINING RING
ADAPTER
GASKET
BOLT
FACE PLATE
THREE-WIRE CORD
ADAPTER MOUNTING PLATE
GASKET
MOTOR
BRUSH
GASKET
RING
HOUSING
BACK PLATE
GROMMET
TAP ASSEMBLY
TUBING
NUT AND BOLT
NUT AND BOLT
GASKET
ROTAMETER
BACKING PLATE
CONDENSER AND CLIP

Figure B1. Exploded view of typical high-volume air sampler parts.

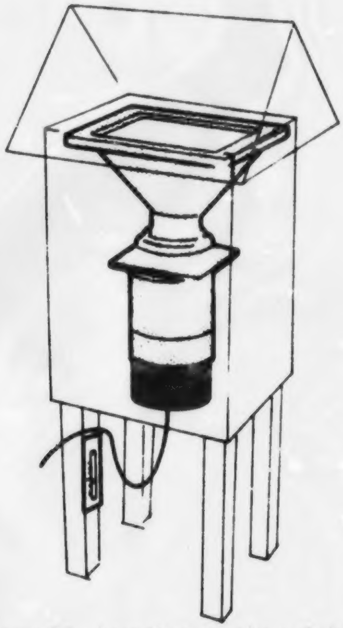

Figure B2. Assembled sampler and shelter.

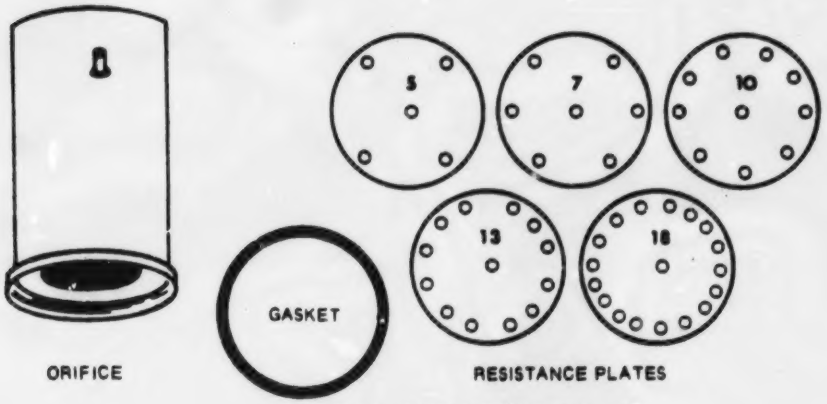
5
7
10
13
16
GASKET
ORIFICE
RESISTANCE PLATES

Figure B3. Orifice calibration unit.

Appendix C

APPENDIX C—MEASUREMENT PRINCIPLE AND CALIBRATION PROCEDURE FOR THE CONTINUOUS MEASUREMENT OF CARBON MONOXIDE IN THE ATMOSPHERE (NON-DISPERSIVE INFRARED SPECTROMETRY)

1. *Principle and applicability.*

1.1 This principle is based on the absorption of infrared radiation by carbon monoxide in a non-dispersive photometer. Both beams pass into matched cells, each containing a selective detector and CO. The CO in the cells absorb infrared radiation only at its characteristic frequencies and the detector is sensitive to those frequencies. With a non-absorbing gas in the reference cell, and with no CO in the sample cell, the signals from both detectors are balanced electronically. Any CO introduced into the sample cell will absorb radiation, which reduces the temperature and pressure in the detector cell and displaces a diaphram. This displacement is detected electronically and amplified to provide an output signal.

1.2 An analyzer based on this principle will be considered a reference method only if it has been designated as a reference method in accordance with Part 53 of this chapter.

2.—6. [Reserved]

7. *Procedure.*

7.1 Calibrate the instrument as described in 8.1. All gases (sample, zero, calibration, and span) must be introduced into the entire analyzer system. Figure C1 shows a typical flow diagram. For specific operating instructions, refer to the manufacturer's manual.

8. *Calibration.*

8.1 *Calibration Curve.* Determine the linearity of the detector response at the operating flow rate and temperature. Prepare a calibration curve and check the curve furnished with the instrument. Introduce zero gas and set the zero control to indicate a recorder reading of zero. Introduce span gas and adjust the span control to indicate the proper value on the recorder scale (e.g. on 0-58 mg./m.^{3} scale, set the 46 mg./m.^{3} standard at 80 percent of the recorder chart). Recheck zero and span until adjustments are no longer necessary. Introduce intermediate calibration gases and plot the values obtained. If a smooth curve is not obtained, calibration gases may need replacement.

9. *Calculations.*

9.1 Determine the concentrations directly from the calibration curve. No calculations are necessary.

9.2 Carbon monoxide concentrations in mg./m.^{3} are converted to p.p.m. as follows:

$$\text{p.p.m.CO} = \text{mg. CO/m.}^3 \times 0.873$$

10. *Bibliography.*

The Intech NDIR-CO Analyzer by Frank McElroy. Presented at the 11th Methods Conference in Air Pollution, University of California, Berkeley, Calif., April 1, 1970.

Jacobs, M. B. et al., J.A.P.C.A. *9, No. 2,* 110-114, August 1959.

MSA LIRA Infrared Gas and Liquid Analyzer Instruction Book, Mine Safety Appliances Co., Pittsburgh, Pa.

Beckman Instruction 1635B, Models 215A, 315A and 415A Infrared Analyzers, Beckman Instrument Company, Fullerton, Calif.

Continuous CO Monitoring System, Model A 5611, Intertech Corp., Princeton, N.J.

Bendix—UNOR Infrared Gas Analyzers, Ronceverte, W. Va.

[36 FR 22384, Nov. 25, 1971, as amended at 40 FR 7043, Feb. 18, 1975]

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Appendix D

APPENDIX D—MEASUREMENT PRINCIPLE AND CALIBRATION PROCEDURE FOR THE MEASUREMENT OF OZONE IN THE ATMOSPHERE

MEASUREMENT PRINCIPLE

1. Ambient air and ethylene are delivered simultaneously to a mixing zone where the ozone in the air reacts with the ethylene to emit light, which is detected by a photomultiplier tube. The resulting photocurrent is amplified and is either read directly or displayed on a recorder.

2. An analyzer based on this principle will be considered a reference method only if it has been designated as a reference method in accordance with Part 53 of this chapter and calibrated as follows:

CALIBRATION PROCEDURE

1. *Principle.* The calibration procedure is based on the photometric assay of ozone (O_3) concentrations in a dynamic flow system. The concentration of O_3 in an absorption cell is determined from a measurement of the amount of 254 nm light absorbed by the sample. This determination requires knowledge of (1) the absorption coefficient (α) of O_3 at 254 nm, (2) the optical path length (l) through the sample, (3) the transmittance of the sample at a wavelength of 254 nm, and (4) the temperature (T) and pressure (P) of the sample. The transmittance is defined as the ratio I/I_0, where I is the intensity of light which passes through the cell and is sensed by the detector when the cell contains an O_3 sample, and I_0 is the intensity of light which passes through the cell and is sensed by the detector when the cell contains zero air. It is assumed that all conditions of the system, except for the contents of the absorption cell, are identical during measurement of I and I_0. The quantities defined above are related by the Beer-Lambert absorption law.

$$\text{Transmittance} = \frac{I}{I_0} = e^{-\alpha c l} \qquad (1)$$

where:

α = absorption coefficient of O_3 at 254 nm = 308 ± 4 atm⁻¹ cm⁻¹ at 0°C and 760 torr.[1,2,3,4,5,6,7]
c = O_3 concentration in atmospheres
l = optical path length in cm

In practice, a stable O_3 generator is used to produce O_3 concentrations over the required range. Each O_3 concentration is determined from the measurement of the transmittance (I/I_0) of the sample at 254 nm with a photometer of path length l and calculated from the equation,

$$c(\text{atm}) = -\frac{1}{\alpha l}(\ln I/I_0) \qquad (2a)$$

or,

$$c(\text{ppm}) = -\frac{10^6}{\alpha l}(\ln I/I_0) \qquad (2b)$$

The calculated O_3 concentrations must be corrected for O_3 losses which may occur in the photometer and for the temperature and pressure of the sample.

2. *Applicability.* This procedure is applicable to the calibration of ambient air O_3 analyzers, either directly or by means of a transfer standard certified by this procedure. Transfer standards must meet the requirements and specifications set forth in Reference 8.

3. *Apparatus.* A complete UV calibration system consists of an ozone generator, an output port or manifold, a photometer, an appropriate source of zero air, and other components as necessary. The configuration must provide a stable ozone concentration at the system output and allow the photometer to accurately assay the output concentration to the precision specified for the photometer (3.1). Figure 1 shows a commonly used configuration and serves to illustrate the calibration procedure which follows. Other configurations may require appropriate variations in the procedural steps. All connections between components in the calibration system downstream of the O_3 generator should be of glass, Teflon, or other relatively inert materials. Additional information regarding the assembly of a UV photometric calibration apparatus is given in Reference 9. For certification of transfer standards which provide their own source of O_3, the transfer standard may replace the O_3 generator and possibly other components shown in Figure 1; see Reference 8 for guidance.

3.1 *UV photometer.* The photometer consists of a low-pressure mercury discharge lamp, (optional) collimation optics, an absorption cell, a detector, and signal-processing electronics, as illustrated in Figure 1. It must be capable of measuring the transmittance, I/I_0, at a wavelength of 254 nm with sufficient precision such that the standard deviation of the concentration measurements does not exceed the greater of 0.005 ppm or 3% of the concentration. Because the low-pressure mercury lamp radiates at several wavelengths, the photometer must incorporate suitable means to assure that no O_3 is generated in the cell by the lamp, and that at least 99.5% of the radiation sensed by the detector is 254 nm radiation. (This can be readily achieved by prudent selection of optical filter and detector response characteristics.) The length of the light path through the absorption cell must be known with an accuracy of at least 99.5%. In addition, the cell and associated plumbing must be designed to minimize loss of O_3 from contact with cell walls and gas handling components. See Reference 9 for additional information.

3.2 *Air flow controllers.* Devices capable of regulating air flows as necessary to meet the output stability and photometer precision requirements.

3.3 *Ozone generator.* Device capable of generating stable levels of O_3 over the required concentration range.

3.4 *Output manifold.* The output manifold should be constructed of glass, Teflon, or other relatively inert material, and should be of sufficient diameter to insure a negligible pressure drop at the photometer connection and other output ports. The system must have a vent designed to insure atmospheric pressure in the manifold and to prevent ambient air from entering the manifold.

3.5 *Two-way valve.* Manual or automatic valve, or other means to switch the photometer flow between zero air and the O_3 concentration.

3.6 *Temperature indicator.* Accurate to ±1°C.

3.7 *Barometer or pressure indicator.* Accurate to ±2 torr.

4. *Reagents.*

4.1 *Zero air.* The zero air must be free of contaminants which would cause a detectable response from the O_3 analyzer, and it should be free of NO, C_2H_4 and other species which react with O_3. A procedure for generating suitable zero air is given in Reference 9. As shown in Figure 1, the zero air supplied to the photometer cell for the I_0 reference measurement must be derived from the same source as the zero air used for generation of the ozone concentration to be assayed (I measurement). When using the photometer to certify a transfer standard having its own source of ozone, see Reference 8 for guidance on meeting this requirement.

5. *Procedure.*

5.1 *General operation.* The calibration photometer must be dedicated exclusively to use as a calibration standard. It should always be used with clean, filtered calibration gases, and never used for ambient air sampling. Consideration should be given to locating the calibration photometer in a clean laboratory where it can be stationary, protected from physical shock, operated by a responsible analyst, and used as a common standard for all field calibrations via transfer standards.

5.2 *Preparation.* Proper operation of the photometer is of critical importance to the accuracy of this procedure. The following steps will help to verify proper operation. The steps are not necessarily required prior to each use of the photometer. Upon initial operation of the photometer, these steps should be carried out frequently, with all quantitative results or indications recorded in a chronological record either in tabular form or plotted on a graphical chart. As the performance and stability record of the photometer is established, the frequency of these steps may be reduced consistent with the documented stability of the photometer.

5.2.1 *Instruction manual:* Carry out all set up and adjustment procedures or checks as described in the operation or instruction manual associated with the photometer.

5.2.2 *System check:* Check the photometer system for integrity, leaks, cleanliness, proper flowrates, etc. Service or replace filters and zero air scrubbers or other consumable materials, as necessary.

5.2.3 *Linearity:* Verify that the photometer manufacturer has adequately established that the linearity error of the photometer is less than 3%, or test the linearity by dilution as follows: Generate and assay an O_3 concentration near the upper range limit of the system (0.5 or 1.0 ppm), then accurately dilute that concentration with zero air and reassay it. Repeat at several different dilution ratios. Compare the assay of the original concentration with the assay of the diluted concentration divided by the dilution ratio, as follows

$$E = \frac{A_1 - A_2/R}{A_1} \times 100\% \qquad (3)$$

where:

E = linearity error, percent
A_1 = assay of the original concentration
A_2 = assay of the diluted concentration
R = dilution ratio = flow of original concentration divided by the total flow

The linearity error must be less than 5%. Since the accuracy of the measured flowrates will affect the linearity error as measured this way, the test is not necessarily conclusive. Additional information on verifying linearity is contained in Reference 9.

5.2.4 *Intercomparison:* When possible, the photometer should be occasionally intercompared, either directly or via transfer standards, with calibration photometers used by other agencies or laboratories.

5.2.5 *Ozone losses:* Some portion of the O_3 may be lost upon contact with the photometer cell walls and gas handling components. The magnitude of this loss must be determined and used to correct the calculated O_3 concentration. This loss must not exceed 5%. Some guidelines for quantitatively determining this loss are discussed in Reference 9.

5.3 *Assay of O_3* concentrations.

5.3.1 Allow the photometer system to warm up and stabilizer.

5.3.2 Verify that the flowrate through the photometer absorption cell, F allows the cell to be flushed in a reasonably short period of time (2 liter/min is a typical flow). The precision of the measurements is inversely related to the time required for flushing, since the photometer drift error increases with time.

5.3.3 Insure that the flowrate into the output manifold is at least 1 liter/min greater than the total flowrate required by the photometer and any other flow demand connected to the manifold.

5.3.4 Insure that the flowrate of zero air, F_z, is at least 1 liter/min greater than the flowrate required by the photometer.

5.3.5 With zero air flowing in the output manifold, actuate the two-way valve to allow the photometer to sample first the manifold zero air, then F_z. The two photometer readings must be equal ($I = I_o$).

Note: In some commercially available photometers, the operation of the two-way valve and various other operations in section 5.3 may be carried out automatically by the photometer.

5.3.6 Adjust the O_3 generator to produce an O_3 concentration as needed.

5.3.7 Actuate the two-way valve to allow the photometer to sample zero air until the absorption cell is thoroughly flushed and record the stable measured value of I_o.

5.3.8 Actuate the two-way valve to allow the photometer to sample the ozone concentration until the absorption cell is thoroughly flushed and record the stable measured value of I.

5.3.9 Record the temperature and pressure of the sample in the photometer absorption cell. (See Reference 9 for guidance.)

5.3.10 Calculate the O_3 concentration from equation 4. An average of several determinations will provide better precision.

$$[O_3]_{OUT} = \left(\frac{-1}{\alpha l} \ln \frac{I}{I_0}\right) \left(\frac{T}{273}\right) \left(\frac{760}{P}\right) \times \frac{10^6}{L} \qquad (4)$$

where:

$[O_3]_{OUT}$ = O_3 concentration, ppm
α = absorption coefficient of O_3 at 254 nm = 308 atm^{-1} cm^{-1} at 0°C and 760 torr
l = optical path length, cm
T = sample temperature, K
P = sample pressure, torr
L = correction factor for O_3 losses from 5.2.5 = (1-fraction O_3 lost).

Note: Some commercial photometers may automatically evaluate all or part of equation 4. It is the operator's responsibility to verify that all of the information required for equation 4 is obtained, either automatically by the photometer or manually. For "automatic" photometers which evaluate the first term of equation 4 based on a linear approximation, a manual correction may be required, particularly at higher O_3 levels. See the photometer instruction manual and Reference 9 for guidance.

5.3.11 Obtain additional O_3 concentration standards as necessary by repeating steps 5.3.6 to 5.3.10 or by Option 1.

5.4 *Certification of transfer standards.* A transfer standard is certified by relating the output of the transfer standard to one or more ozone standards as determined according to section 5.3. The exact procedure varies depending on the nature and design of the transfer standard. Consult Reference 8 for guidance.

5.5 *Calibration of ozone analyzers.* Ozone analyzers are calibrated as follows, using ozone standards obtained directly according to section 5.3 or by means of a certified transfer standard.

5.5.1 Allow sufficient time for the O_3 analyzer and the photometer or transfer standard to warmup and stabilize.

5.5.2 Allow the O_3 analyzer to sample zero air until a stable response is obtained and adjust the O_3 analyzer's zero control. Offsetting the analyzer's zero adjustment to +5% of scale is recommended to facilitate observing negative zero drift. Record the stable zero air response as "Z".

5.5.3 Generate an O_3 concentration standard of approximately 80% of the desired upper range limit (URL) of the O_3 analyzer. Allow the O_3 analyzer to sample this O_3 concentration standard until a stable response is obtained.

5.5.4 Adjust the O_3 analyzer's span control to obtain a convenient recorder response as indicated below:

$$\text{recorder response (\% scale)} = \left(\frac{[O_3]_{OUT}}{URL} \times 100\right) + Z \qquad (5)$$

where:

URL = upper range limit of the O_3 analyzer, ppm
Z = recorder response with zero air, % scale

Record the O_3 concentration and the corresponding analyzer response. If substantial adjustment of the span control is necessary, recheck the zero and span adjustments by repeating steps 5.5.2 to 5.5.4.

5.5.5 Generate several other O_3 concentration standards (at least 5 others are recommended) over the scale range of the O_3 analyzer by adjusting the O_3 source or by Option 1. For each O_3 concentration standard, record the O_3 and the corresponding analyzer response.

5.5.6 Plot the O_3 analyzer responses versus the corresponding O_3 concentrations and draw the O_3 analyzer's calibration curve or calculate the appropriate response factor.

5.5.7 *Option 1:* The various O_3 concentrations required in steps 5.3.11 and 5.5.5 may be obtained by dilution of the O_3 concentration generated in steps 5.3.6 and 5.5.3. With this option, accurate flow measurements are required. The dynamic calibration system may be modified as shown in Figure 2 to allow for dilution air to be metered in downstream of the O_3 generator. A mixing chamber between the O_3 generator and the output manifold is also required. The flowrate through the O_3 generator (F_o) and the dilution air flowrate (F_D) are measured with a reliable flow or volume standard traceable to NBS. Each O_3 concentration generated by dilution is calculated from:

$$[O_3]'_{OUT} = [O_3]_{OUT} \left(\frac{F_O}{F_O + F_D}\right) \qquad (6)$$

where:

$[O_3]'_{OUT}$ = diluted O_3 concentration, ppm
F_o = flowrate through the O_3 generator, liter/min
F_D = diluent air flowrate, liter/min

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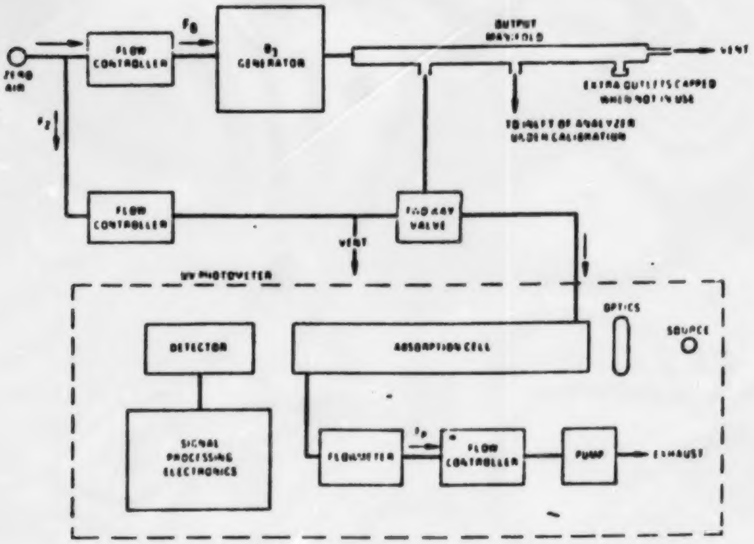
ZERO AIR
FLOW CONTROLLER
F_O
O_3 GENERATOR
OUTPUT MANIFOLD
VENT
EXTRA OUTLETS CAPPED WHEN NOT IN USE
TO INLET OF ANALYZER UNDER CALIBRATION
F_Z
FLOW CONTROLLER
TWO-WAY VALVE
VENT
UV PHOTOMETER
OPTICS
SOURCE
DETECTOR
ABSORPTION CELL
SIGNAL PROCESSING ELECTRONICS
FLOWMETER
F_P
FLOW CONTROLLER
PUMP
EXHAUST

Figure 1 Schematic diagram of a typical UV photometric calibration system

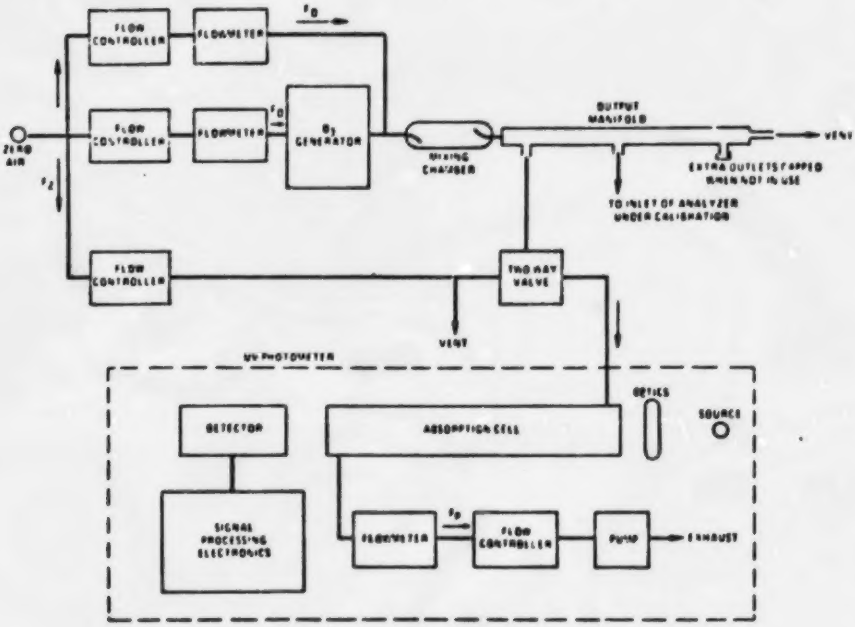
FLOW CONTROLLER
FLOWMETER
F_D
ZERO AIR
FLOW CONTROLLER
FLOWMETER
F_O
O_3 GENERATOR
MIXING CHAMBER
OUTPUT MANIFOLD
VENT
EXTRA OUTLETS CAPPED WHEN NOT IN USE
TO INLET OF ANALYZER UNDER CALIBRATION
F_Z
FLOW CONTROLLER
TWO-WAY VALVE
VENT
UV PHOTOMETER
OPTICS
SOURCE
DETECTOR
ABSORPTION CELL
SIGNAL PROCESSING ELECTRONICS
FLOWMETER
F_P
FLOW CONTROLLER
PUMP
EXHAUST

Figure 2 Schematic diagram of a typical UV photometric calibration system (OPTION 1)

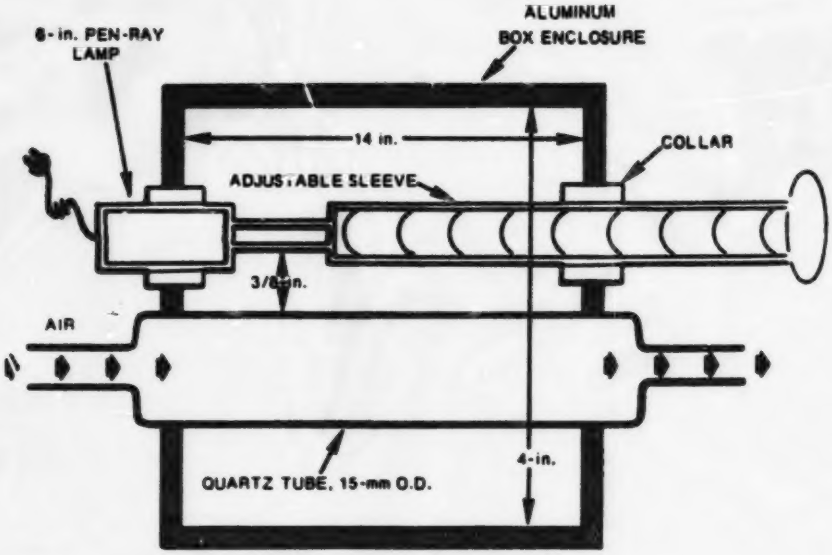
6-in. PEN-RAY LAMP
ALUMINUM BOX ENCLOSURE
14 in.
COLLAR
ADJUSTABLE SLEEVE
3/8-in.
AIR
4-in.
QUARTZ TUBE, 15-mm O.D.

Figure D2. Ozone source.

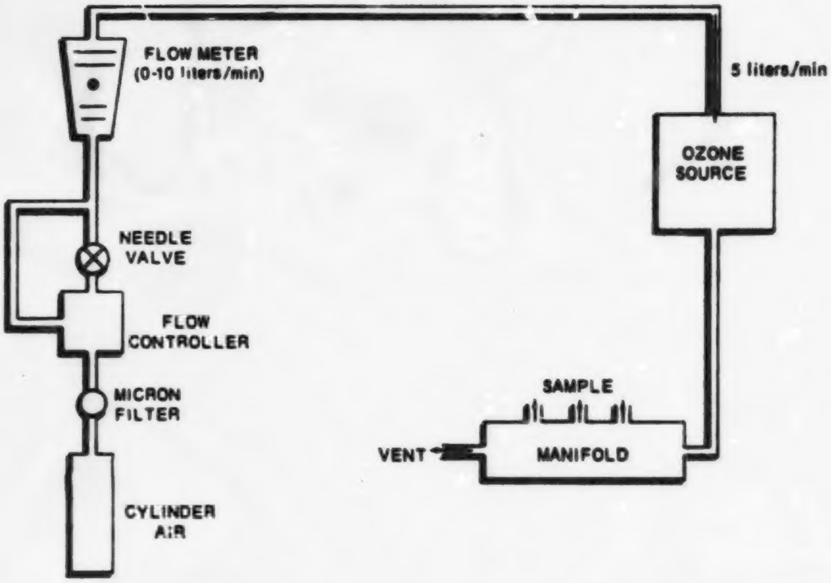
FLOW METER (0-10 liters/min)
5 liters/min
OZONE SOURCE
NEEDLE VALVE
FLOW CONTROLLER
MICRON FILTER
SAMPLE
VENT
MANIFOLD
CYLINDER AIR

Figure D3. Ozone calibration air supply, source, and manifold system.

Appendix E

APPENDIX E—REFERENCE METHOD FOR DETERMINATION OF HYDROCARBONS CORRECTED FOR METHANE

1. *Principle and Applicability.*

1.1 Measured volumes of air are delivered semicontinuously (4 to 12 times per hour) to a hydrogen flame ionization detector to measure its total hydrocarbon (THC) content. An aliquot of the same air sample is introduced into a stripper column which removes water, carbon dioxide, and hydrocarbons other than methane. Methane and carbon monoxide are passed quantitatively to a gas chromatographic column where they are separated. The methane is eluted first, and is passed unchanged through a catalytic reduction tube into the flame ionization detector. The carbon monoxide is eluted into the catalytic reduction tube where it is reduced to methane before passing through the flame ionization detector. Between analyses the stripper column is backflushed to prepare it for subsequent analysis. Hydrocarbon concentrations corrected for methane are determined by subtracting the methane value from the total hydrocarbon value.

Two modes of operation are possible: (1) A complete chromatographic analysis showing the continuous output from the detector for each sample injection; (2) The system is programed for automatic zero and span to display selected band widths of the chromatogram. The peak height is then used as the measure of the concentration. The former operation is referred to as the chromatographic or spectro mode and the latter as the barographic or "normal" mode depending on the make of analyzer.

1.2 The method is applicable to the semicontinuous measurement of hydrocarbons corrected for methane in ambient air. The carbon monoxide measurement, which is simultaneously obtained in this method, is not required in making measurements of hydrocarbons corrected for methane and will not be dealt with here.

2. *Range and Sensitivity.*

2.1 Instruments are available with various range combinations. For atmospheric analysis the THC range is 0-13.1 mg./m.^{3} (0-20 p.p.m.) carbon (as CH_4) and the methane range is 0-6.55 mg./m.^{3} (0-10 p.p.m.). For special applications, lower ranges are available and in these applications the range for THC is 0-1.31 mg./m.^{3} (0-2 p.p.m.) carbon (as CH_4) and for methane the range is 0-1.31 mg./m.^{3} (0-2 p.p.m.).

2.2 For the higher, atmospheric analysis ranges the sensitivity for THC is 0.065 mg./m.^{3} (0.1 p.p.m.) carbon (as CH_4) and for methane the sensitivity is 0.033 mg./m.^{3} (0.05 p.p.m.). For the lower, special analysis ranges the sensitivity is 0.016 mg./m.^{3} (0.025 p.p.m.) for each gas.

3. *Interferences.*

3.1 No interference in the methane measurement has been observed. The THC measurement typically includes all or a portion of what is generally classified as the air peak interference. This effect is minimized by proper plumbing arrangements or is negated electronically.

4. *Precision, Accuracy, and Stability.*

4.1 Precision determined with calibration gases is ±0.5 percent of full scale in the higher, atmospheric analysis ranges.

4.2 Accuracy is dependent on instrument linearity and absolute concentration of the calibration gases. An accuracy of 1 percent of full scale in the higher, atmospheric analysis ranges and 2 percent of full scale in the lower, special analysis ranges can be obtained.

4.3 Variations in ambient room temperature can cause changes in performance characteristics. This is due to shifts in oven temperature, flow rates, and pressure with ambient temperature change. The instrument should meet performance specifications with room temperature changes of ±3° C. Baseline drift is automatically corrected in the barographic mode.

5. *Apparatus.* 5.1 *Commercially Available THC, CH_4, and CO Analyzer.* Instruments should be installed on location and demonstrated, preferably by the manufacturer, or his representative, to meet or exceed manufacturer's specifications and those described in this method.

5.2 *Sample Introduction System.* Pump, flow control valves, automatic switching valves, and flowmeter.

5.3 *Filter (In-line).* A binder-free, glass-fiber filter with a porosity of 3 to 5 microns should be immediately downstream from the sample pump.

5.4 *Stripper or Precolumn.* Located outside of the oven at ambient temperature. The column should be repacked or replaced after the equivalent of 2 months of continuous operation.

5.5 *Oven.* For containing the analytical column and catalytic converter. The oven should be capable of maintaining an elevated temperature constant within ±0.5° C. The specific temperature varies with instrument manufacturer.

6. *Reagents.*

6.1 *Combustion Gas.* Air containing less than 1.3 mg./m.^{3} (2 p.p.m.) hydrocarbon as methane.

6.2 *Fuel.* Hydrogen or a mixture of hydrogen and inert gas containing less than 0.065 mg./m.^{3} (0.1 p.p.m.) hydrocarbons as methane.

6.3 *Carrier Gas.* Helium, nitrogen, air or hydrogen containing less than 0.005 mg./m.^{3} (0.1 p.p.m.) hydrocarbons as methane.

6.4 *Zero Gas.* Air containing less than 0.065 mg./m.^{3} (0.1 p.p.m.) total hydrocarbons as methane.

6.5 *Calibration Gases.* Gases needed for linearity checks (peak heights) are determined by the ranges used. Calibration gases corresponding to 10, 20, 40, and 80 percent of full scale are needed. Gases must be provided with certification or guaranteed analysis. Methane is used for both the total hydrocarbon measurement and methane measurement.

6.6 *Span Gas.* The calibration gas corresponding to 80 percent of full scale is used to span the instrument.

7. *Procedure.*

7.1 Calibrate the instrument as described in 8.1. Introduce sample into the system under the same conditions of pressure and flow rates as are used in calibration. (The pump is bypassed only when pressurized cylinder gases are used.) Figure E1 shows a typical flow diagram; for specific operating instructions refer to manufacturer's manual.

8. *Calibration.*

8.1 *Calibration Curve.* Determine the linearity of the system for THC and methane in the barographic mode by introducing zero gas and adjusting the respective zeroing controls to indicate a recorder reading of zero. Introduce the span gas and adjust the span control to indicate the proper value on the recorder scale. Recheck zero and span until adjustments are no longer necessary. Introduce intermediate calibration gases and plot the values obtained. If a smooth curve is not obtained, calibration gases may need replacement.

9. *Calculation.*

9.1 Determine concentrations of total hydrocarbons (as CH_4) and CH_4, directly from the calibration curves. No calculations are necessary.

9.2 Determine concentration of hydrocarbons corrected for methane by subtracting the methane concentration from the total hydrocarbon concentration.

9.3 Conversion between p.p.m. and mg./m.^{3} values for total hydrocarbons (as CH_4) methane and hydrocarbons corrected for methane are made as follows:

$$\text{p.p.m. carbon (as } CH_4) = [\text{mg. carbon (as } CH_4)/\text{m.}^3] \times 1.53$$

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ADDENDA

A. *Suggested Performance Specifications for Atmospheric Analyzers for Hydrocarbons Corrected for Methane:*

Range (minimum)	0-3 mg/m^3 (0-5 p.p.m.) THC 0-3 mg/m^3 (0-5 p.p.m.) CH_4
Output (minimum)	0-10 mv. full scale
Minimum detectable sensitivity	0.1 p.p.m. THC 0.1 p.p.m. CH_4
Zero drift (maximum)	Not to exceed 1 percent/24 hours.
Span drift (maximum)	Not to exceed 1 percent/24 hours.
Precision (minimum)	±0.5 percent.
Operational period (minimum)	3 days
Operating temperature range (minimum)	5-40° C
Operating humidity range (minimum)	10-100 percent
Linearity (maximum)	1 percent of full scale

B. *Suggested Definitions of Performance Specifications:*

Range—The minimum and maximum measurement limits.

Output—Electrical signal which is proportional to the measurement; intended for connection to readout or data processing devices. Usually expressed as millivolts or milliamps full scale at a given impedence.

Full Scale—The maximum measuring limit for a given range.

Minimum Detectable Sensitivity—The smallest amount of input concentration that can be detected as the concentration approaches zero.

Accuracy—The degree of agreement between a measured value and the true value; usually expressed at ± percent of full scale.

Lag Time—The time interval from a step change in input concentration at the instrument inlet to the first corresponding change in the instrument output.

Time to 90 Percent Response—The time interval from a step change in the input concentration at the instrument inlet to a reading of 90 percent of the ultimate recorded concentration.

Rise Time (90 percent)—The interval between initial response time and time to 90 percent response after a step decrease in the inlet concentration.

Zero Drift—The change in instrument output over a stated time period, usually 24 hours, of unadjusted continuous operation, when the input concentration is zero; usually expressed as percent full scale.

Span Drift—The change in instrument output over a stated time period, usually 24 hours, of unadjusted continuous operation, when the input concentration is a stated upscale value; usually expressed as percent full scale.

Precision—The degree of agreement between repeated measurements of the same concentration. It is expressed as the average deviation of the single results from the mean.

Operational Period—The period of time over which the instrument can be expected to operate unattended within specifications.

Noise—Spontaneous deviations from a mean output not caused by input concentration changes.

Interference—An undesired positive or negative output caused by a substance other than the one being measured.

Interference Equivalent—The portion of indicated input concentration due to the presence of an interferent.

Operating Temperature Range—The range of ambient temperatures over which the instrument will meet all performance specifications.

Operating Humidity Range—The range of ambient relative humidity over which the instrument will meet all performance specifications.

Linearity—The maximum deviation between an actual instrument reading and the reading predicted by a straight line drawn between upper and lower calibration points.

Appendix F

APPENDIX F—MEASUREMENT PRINCIPLE AND CALIBRATION PROCEDURE FOR THE MEASUREMENT OF NITROGEN DIOXIDE IN THE ATMOSPHERE (GAS PHASE CHEMILUMINESCENCE)

Principle and Applicability

1. Atmospheric concentrations of nitrogen dioxide (NO_2) are measured indirectly by photometrically measuring the light intensity, at wavelengths greater than 600 nanometers, resulting from the chemiluminescent reaction of nitric oxide (NO) with ozone (O_3). (*1,2,3*) NO_2 is first quantitatively reduced to NO(*4,5,6*) by means of a converter. NO, which commonly exists in ambient air together with NO_2, passes through the converter unchanged causing a resultant total NO_x concentration equal to NO+NO_2. A sample of the input air is also measured without having passed through the converter. This latter NO measurement is subtracted from the former measurement (NO+NO_2) to yield the final NO_2 measurement. The NO and NO+NO_2 measurements may be made concurrently with dual systems, or cyclically with the same system provided the cycle time does not exceed 1 minute.

2. *Sampling considerations.*

2.1 Chemiluminescence NO/NO_x/NO_2 analyzers will respond to other nitrogen containing compounds, such as peroxyacetyl nitrate (PAN), which might be reduced to NO in the thermal converter. (*7*) Atmospheric concentrations of these potential interferences are generally low relative to NO_2 and valid NO_2 measurements may be obtained. In certain geographical areas, where the concentration of these potential interferences is known or suspected to be high relative to NO_2, the use of an equivalent method for the measurement of NO_2 is recommended.

2.2 The use of integrating flasks on the sample inlet line of chemiluminescence NO/NO_x/NO_2 analyzers is optional and left to couraged. The sample residence time between the sampling point and the analyzer should be kept to a minimum to avoid erroneous NO_2 measurements resulting from the reaction of ambient levels of NO and O_3 in the sampling system.

2.3 The use of particulate filters on the sample inlet line of chemiluminescence NO/NO_x/NO_2 analyzers is optional and left to the discretion of the user or the manufacturer. Use of the filter should depend on the analyzer's susceptibility to interference, malfunction, or damage due to particulates. Users are cautioned that particulate matter concentrated on a filter may cause erroneous NO_2 measurements and therefore filters should be changed frequently.

3. An analyzer based on this principle will be considered a reference method only if it has been designated as a reference method in accordance with Part 53 of this chapter.

Calibration

1. *Alternative A*—Gas phase titration (GPT) of an NO standard with O_3.

Major equipment required: Stable O_3 generator. Chemiluminescence NO/NO_x/NO_2 analyzer with strip chart recorder(s). NO concentration standard.

1.1 Principle. This calibration technique is based upon the rapid gas phase reaction between NO and O_3 to produce stoichiometric quantities of NO_2 in accordance with the following equation: (*8*)

$$NO + O_3 \rightarrow NO_2 + O_2 \qquad (1)$$

The quantitative nature of this reaction is such that when the NO concentration is known, the concentration of NO_2 can be determined. Ozone is added to excess NO in a dynamic calibration system, and the NO channel of the chemiluminescence NO/NO_x/NO_2 analyzer is used as an indicator of changes in NO concentration. Upon the addition of O_3, the decrease in NO concentration observed on the calibrated NO channel is equivalent to the concentration of NO_2 produced. The amount of NO_2 generated may be varied by adding variable amounts of O_3 from a stable uncalibrated O_3 generator. (*9*)

1.2 Apparatus. Figure 1, a schematic of a typical GPT apparatus, shows the suggested configuration of the components listed below. All connections between components in the calibration system downstream from the O_3 generator should be of glass, Teflon®, or other non-reactive material.

1.2.1 Air flow controllers. Devices capable of maintaining constant air flows within ±2% of the required flowrate.

1.2.2 NO flow controller. A device capable of maintaining constant NO flows within ±2% of the required flowrate. Component parts in contact with the NO should be of a non-reactive material.

1.2.3 Air flowmeters. Calibrated flowmeters capable of measuring and monitoring air flowrates with an accuracy of ±2% of the measured flowrate.

1.2.4 NO flowmeter. A calibrated flowmeter capable of measuring and monitoring NO flowrates with an accuracy of ±2% of the measured flowrate. (Rotameters have been reported to operate unreliably when measuring low NO flows and are not recommended.)

1.2.5 Pressure regulator for standard NO cylinder. This regulator must have a nonreactive diaphragm and internal parts and a suitable delivery pressure.

1.2.6 Ozone generator. The generator must be capable of generating sufficient and stable levels of O_3 for reaction with NO to generate NO_2 concentrations in the range required. Ozone generators of the electric discharge type may produce NO and NO_2 and are not recommended.

1.2.7 Valve. A valve may be used as shown in Figure 1 to divert the NO flow when zero air is required at the manifold. The valve should be constructed of glass, Teflon®, or other nonreactive material.

1.2.8 Reaction chamber. A chamber, constructed of glass, Teflon®, or other nonreactive material, for the quantitative reaction of O_3 with excess NO. The chamber should be of sufficient volume (V_{RC}) such that the residence time (t_R) meets the requirements specified in 1.4. For practical reasons, t_R should be less than 2 minutes.

1.2.9 Mixing chamber. A chamber constructed of glass, Teflon®, or other nonreactive material and designed to provide thorough mixing of reaction products and diluent air. The residence time is not critical when the dynamic parameter specification given in 1.4 is met.

1.2.10 Output manifold. The output manifold should be constructed of glass, Teflon®, or other non-reactive material and should be of sufficient diameter to insure an insignificant pressure drop at the analyzer connection. The system must have a vent designed to insure atmospheric pressure at the manifold and to prevent ambient air from entering the manifold.

1.3 Reagents.

1.3.1 NO concentration standard. Cylinder containing 50 to 100 ppm NO in N_2 with less than 1 ppm NO_2. The cylinder must be traceable to a National Bureau of Standards NO in N_2 Standard Reference Material (SRM 1683 or SRM 1684) or NO_2 Standard Reference Material (SRM 1629). Procedures for certifying the NO cylinder (working standard) against an NBS traceable NO or NO_2 standard and for determining the amount of NO_2 impurity are given in reference 13. The cylinder should be recertified on a regular basis as determined by the local quality control program.

1.3.2 Zero air. Air, free of contaminants which will cause a detectable response on the NO/NO_x/NO_2 analyzer or which might react with either NO, O_3, or NO_2 in the gas phase titration. A procedure for generating zero air is given in *reference 13*.

1.4 Dynamic parameter specification.

1.4.1 The O_3 generator air flowrate (F_O) and NO flowrate (F_{NO}) (see Figure 1) must be adjusted such that the following relationship holds:

$$P_R = [NO]_{RC} \times t_R \;\; 2.75 \text{ ppm-minutes} \qquad (2)$$

$$[NO]_{RC} = [NO]_{STD} \left(\frac{F_{NO}}{F_O + F_{NO}} \right) \qquad (3)$$

$$t_R = \frac{V_{RC}}{F_O + F_{NO}} < 2 \text{ minutes} \qquad (4)$$

where:

P_R = dynamic parameter specification, determined empirically, to insure complete reaction of the available O_3, ppm-minute
$[NO]_{RC}$ = NO concentration in the reaction chamber, ppm
t_R = residence time of the reactant gases in the reaction chamber, minute
$[NO]_{STD}$ = concentration of the undiluted NO standard, ppm
F_{NO} = NO flowrate, scm^3/min
F_O = O_3 generator air flowrate, scm^3/min
V_{RC} = volume of the reaction chamber, scm^3

1.4.2 The flow conditions to be used in the GPT system are determined by the following procedure:

(a) Determine F_T, the total flow required at the output manifold (F_T = analyzer demand plus 10 to 50% excess).

(b) Establish $[NO]_{OUT}$ as the highest NO concentration (ppm) which will be required at the output manifold. $[NO]_{OUT}$ should be approximately equivalent to 90% of the upper range limit (*URL*) of the NO_2 concentration range to be covered.

(c) Determine F_{NO} as

$$F_{NO} = \frac{[NO]_{OUT} \times F_T}{[NO]_{STD}} \qquad (5)$$

(d) Select a convenient or available reaction chamber volume. Initially, a trial V_{RC} may be selected to be in the range of approximately 200 to 500 scm^3.

(e) Compute FO as

$$F_O = \sqrt{\frac{[NO]_{STD} \times F_{NO} \times V_{RC}}{2.75}} - F_{NO} \qquad (6)$$

(f) Compute t_R as

$$t_R = \frac{V_{RC}}{F_O - F_{NO}} \qquad (7)$$

Verify that $t_R < 2$ minutes. If not, select a reaction chamber with a smaller V_{RC}.

(g) Compute the diluent air flowrate as

$$F_D = F_T - F_O - F_{NO} \qquad (8)$$

where:

F_D = diluent air flowrate, scm ^{3}/min

(h) If F_O turns out to be impractical for the desired system, select a reaction chamber having a different V_{RC} and recompute F_O and F_D.

NOTE: A dynamic parameter lower than 2.75 ppm-minutes may be used if it can be determined empirically that quantitative reaction of O_3 with NO occurs. A procedure for making this determination as well as a more detailed discussion of the above requirements and other related considerations is given in reference 13.

1.5 *Procedure.*

1.5.1 Assemble a dynamic calibration system such as the one shown in Figure 1.

1.5.2 Insure that all flowmeters are calibrated under the conditions of use against a reliable standard such as a soap-bubble meter or wet-test meter. All volumetric flowrates should be corrected to 25° C and 760 mm Hg. A discussion on the calibration of flowmeters is given in reference 13.

1.5.3 Precautions must be taken to remove O_2 and other contaminants from the NO pressure regulator and delivery system prior to the start of calibration to avoid any conversion of the standard NO to NO_2. Failure to do so can cause significant errors in calibration. This problem may be minimized by (1) carefully evacuating the regulator, when possible, after the regulator has been connected to the cylinder and before opening the cylinder valve; (2) thoroughly flushing the regulator and delivery system with NO after opening the cylinder valve; (3) not removing the regulator from the cylinder between calibrations unless absolutely necessary. Further discussion of these procedures is given in reference 13.

1.5.4 Select the operating range of the $NO/NO_x/NO_2$ analyzer to be calibrated. In order to obtain maximum precision and accuracy for NO_2 calibration, all three channels of the analyzer should be set to the same range. If operation of the NO and NO_x channels on higher ranges is desired, subsequent recalibration of the NO and NO_x channels on the higher ranges is recommended.

NOTE: Some analyzer designs may require identical ranges for NO, NO_x, and NO_2 during operation of the analyzer.

1.5.5 Connect the recorder output cable(s) of the $NO/NO_x/NO_2$ analyzer to the input terminals of the strip chart recorder(s). All adjustments to the analyzer should be performed based on the appropriate strip chart readings. References to analyzer responses in the procedures given below refer to recorder responses.

1.5.6 Determine the GPT flow conditions required to meet the dynamic parameter specification as indicated in 1.4.

1.5.7 Adjust the diluent air and O_3 generator air flows to obtain the flows determined in 1.4.2. The total air flow must exceed the total demand of the analyzer(s) connected to the output manifold to insure that no ambient air is pulled into the manifold vent. Allow the analyzer to sample zero air until stable NO, NO_x, and NO_2 responses are obtained. After the responses have stabilized, adjust the analyzer zero control(s).

NOTE: Some analyzers may have separate zero controls for NO, NO_x, and NO_2. Other analyzers may have separate zero controls only for NO and NO_x, while still others may have only one zero control common to all three channels.

Offsetting the analyzer zero adjustments to +5 percent of scale is recommended to facilitate observing negative zero drift. Record the stable zero air responses as Z_{NO}, Z_{NOX}, and Z_{NO_2}.

1.5.8 Preparation of NO and NO_x calibration curves.

1.5.8.1 Adjustment of NO span control. Adjust the NO flow from the standard NO cylinder to generate an NO concentration of approximately 80 percent of the upper range limit (*URL*) of the NO range. This exact NO concentration is calculated from:

$$[NO]_{OUT} = \frac{F_{NO} \times [NO]_{STD}}{F_{NO} + F_O + F_D} \qquad (9)$$

where:

$[NO]_{OUT}$ = diluted NO concentration at the output manifold, ppm

Sample this NO concentration until the NO and NO_x responses have stabilized. Adjust the NO span control to obtain a recorder response as indicated below:

recorder response (percent scale)

$$= \left(\frac{[NO]_{OUT}}{URL} \times 100\right) + Z_{NO} \qquad (10)$$

where:

URL = nominal upper range limit of the NO channel, ppm

NOTE: Some analyzers may have separate span controls for NO, NO_x, and NO_2. Other analyzers may have separate span controls only for NO and NO_x, while still others may have only one span control common to all three channels. When only one span control is available, the span adjustment is made on the NO channel of the analyzer.

If substantial adjustment of the NO span control is necessary, it may be necessary to recheck the zero and span adjustments by repeating steps 1.5.7 and 1.5.8.1. Record the NO concentration and the analyzer's NO response.

1.5.8.2 Adjustment of NO_x span control. When adjusting the analyzer's NO_x span control, the presence of any NO_2 impurity in the standard NO cylinder must be taken into account. Procedures for determining the amount of NO_2 impurity in the standard NO cylinder are given in reference 13. The exact NO_x concentration is calculated from:

$$[NO_x]_{OUT} = \frac{F_{NO} \times ([NO]_{STD} + [NO_2]_{IMP})}{F_{NO} + F_O + F_D} \qquad (11)$$

where:

$[NO_x]_{OUT}$ = diluted NO_x concentration at the output manifold, ppm

$[NO_2]_{IMP}$ = concentration of NO_2 impurity in the standard NO cylinder, ppm

Adjust the NO_x span control to obtain a recorder response as indicated below:

recorder response (% scale)

$$= \left(\frac{[NO_x]_{OUT}}{URL} \times 100\right) + Z_{NO_x} \qquad (12)$$

NOTE: If the analyzer has only one span control, the span adjustment is made on the NO channel and no further adjustment is made here for NO_x.

If substantial adjustment of the NO_x span control is necessary, it may be necessary to recheck the zero and span adjustments by repeating steps 1.5.7 and 1.5.8.2. Record the NO_x concentration and the analyzer's NO_x response.

1.5.8.3 Generate several additional concentrations (at least five evenly spaced points across the remaining scale are suggested to verify linearity) by decreasing F_{NO} or increasing F_D. For each concentration generated, calculate the exact NO and NO_x concentrations using equations (9) and (11) respectively. Record the analyzer's NO and NO_x responses for each concentration. Plot the analyzer responses versus the respective calculated NO and NO_x concentrations and draw or calculate the NO and NO_x calibration curves. For subsequent calibrations where linearity can be assumed, these curves may be checked with a two-point calibration consisting of a zero air point and NO and NO_x concentrations of approximately 80% of the *URL*.

1.5.9 *Preparation of NO_2 calibration curve.*

1.5.9.1 Assuming the NO_2 zero has been properly adjusted while sampling zero air in step 1.5.7, adjust F_O and F_D as determined in 1.4.2. Adjust F_{NO} to generate an NO concentration near 90% of the *URL* of the NO range. Sample this NO concentration until the NO and NO_x responses have stabilized. Using the NO calibration curve obtained in 1.5.8, measure and record the NO concentration as $[NO]_{orig}$. Using the NO_x calibration curve obtained in 1.5.8, measure and record the NO_x concentration as $[NO_x]_{orig}$.

1.5.9.2 Adjust the O_3 generator to generate sufficient O_3 to produce a decrease in the NO concentration equivalent to approximately 80% of the URL of the NO_2 range.

NOTE: If the analyzer has only one or two span controls, the span adjustments are made on the NO channel or NO and NO_x channels and no further adjustment is made here for NO_2.

If substantial adjustment of the NO_2 span control is necessary, it may be necessary to recheck the zero and span adjustments by repeating steps 1.5.7 and 1.5.9.3. Record the NO_2 concentration and the corresponding analyzer NO_2 and NO_x responses.

1.5.9.4 Maintaining the same F_{NO}, F_O, and F_D as in 1.5.9.1, adjust the ozone generator to obtain several other concentrations of NO_2 over the NO_2 range (at least five evenly spaced points across the remaining scale are suggested). Calculate each NO_2 concentration using equation (13) and record the corresponding analyzer NO_2 and NO_x responses. Plot the analyzer's NO_2 responses versus the corresponding calculated NO_2 concentrations and draw or calculate the NO_2 calibration curve.

1.5.10 *Determination of converter efficiency.*

1.5.10.1 For each NO_2 concentration generated during the preparation of the NO_2 calibration curve (see 1.5.9) calculate the concentration of NO_2 converted from:

$$[NO_2]_{CONV} = [NO_2]_{OUT} - ([NO_x]_{orig} - [NO_x]_{rem}) \qquad (15)$$

where:

$[NO_2]_{CONV}$ = concentration of NO_2 converted, ppm

$[NO_x]_{orig}$ = original NO_x concentration prior to addition of O_3, ppm

$[NO_x]_{rem}$ = NO_x concentration remaining after addition of O_3, ppm

The decrease must not exceed 90% of the NO concentration determined in step 1.5.9.1. After the analyzer responses have stabilized, record the resultant NO and NO_x concentrations as $[NO]_{rem}$ and $[NO_x]_{rem}$.

1.5.9.3 Calculate the resulting NO_2 concentration from:

$$[NO_2]_{OUT} = [NO]_{orig} - [NO]_{rem} + \frac{F_{NO} \times [NO_2]_{IMP}}{F_{NO} + F_O + F_D} \qquad (13)$$

where:

$[NO_2]_{OUT}$ = diluted NO_2 concentration at the output manifold, ppm

$[NO]_{orig}$ = original NO concentration, prior to addition of O_3, ppm

$[NO]_{rem}$ = NO concentration remaining after addition of O_3, ppm

Adjust the NO_2 span control to obtain a recorder response as indicated below:

$$\text{recorder response (\% scale)} = \left(\frac{[NO_2]_{OUT}}{URL} \times 100\right) + Z_{NO_2} \qquad (14)$$

NOTE: Supplemental information on calibration and other procedures in this method are given in reference 13.

Plot $[NO_2]_{CONV}$ (y-axis) versus $[NO_2]_{OUT}$ (x-axis) and draw or calculate the converter efficiency curve. The slope of the curve times 100 is the average converter efficiency, E_C. The average converter efficiency must be greater than 96%; if it is less than 96%, replace or service the converter.

2. *Alternative B*—NO_2 permeation device.

Major equipment required:

Stable O_3 generator.

Chemiluminescence $NO/NO_x/NO_2$ analyzer with strip chart recorder(s).

NO concentration standard.

NO_2 concentration standard.

2.1 *Principle.* Atmospheres containing accurately known concentrations of nitrogen dioxide are generated by means of a permeation device. (*10*) The permeation device emits NO_2 at a known constant rate provided the temperature of the device is held constant (±0.1° C) and the device has been accurately calibrated at the temperature of use. The NO_2 emitted from the device is diluted with zero air to produce NO_2 concentrations suitable for calibration of the NO_2 channel of the $NO/NO_x/NO_2$ analyzer. An NO concentration standard is used for calibration of the NO and NO_x channels of the analyzer.

2.2 *Apparatus.* A typical system suitable for generating the required NO and NO_2 concentrations is shown in Figure 2. All connections between components downstream from the permeation device should be of glass, Teflon®, or other non-reactive material.

2.2.1 *Air flow controllers.* Devices capable of maintaining constant air flows within ±2% of the required flowrate.

2.2.2 *NO flow controller.* A device capable of maintaining constant NO flows within ±2% of the required flowrate. Component parts in contact with the NO must be of a non-reactive material.

2.2.3 *Air flowmeters.* Calibrated flowmeters capable of measuring and monitoring air flowrates with an accuracy of ±2% of the measured flowrate.

2.2.4 *NO flowmeter.* A calibrated flowmeter capable of measuring and monitoring NO flowrates with an accuracy of ±2% of the measured flowrate. (Rotameters have been reported to operate unreliably when measuring low NO flows and are not recommended.)

2.2.5 *Pressure regulator for standard NO cylinder.* This regulator must have a non-reactive diaphragm and internal parts and a suitable delivery pressure.

2.2.6 *Drier.* Scrubber to remove moisture from the permeation device air system. The use of the drier is optional with NO_2 permeation devices not sensitive to moisture. (Refer to the supplier's instructions for use of the permeation device.)

2.2.7 *Constant temperature chamber.* Chamber capable of housing the NO_2 permeation device and maintaining its temperature to within ±0.1°C.

2.2.8 *Temperature measuring device.* Device capable of measuring and monitoring the temperature of the NO_2 permeation device with an accuracy of ±0.05°C.

2.2.9 *Valves.* A valve may be used as shown in Figure 2 to divert the NO_2 from the permeation device when zero air or NO is required at the manifold. A second valve may be used to divert the NO flow when zero air or NO_2 is required at the manifold.

The valves should be constructed of glass, Teflon®, or other nonreactive material.

2.2.10 *Mixing chamber.* A chamber constructed of glass, Teflon®, or other nonreactive material and designed to provide thorough mixing of pollutant gas streams and diluent air.

2.2.11 *Output manifold.* The output manifold should be constructed of glass, Teflon®, or other non-reactive material and should be of sufficient diameter to insure an insignificant pressure drop at the analyzer connection. The system must have a vent designed to insure atmospheric pressure at the manifold and to prevent ambient air from entering the manifold.

2.3 *Reagents.*

2.3.1 *Calibration standards.* Calibration standards are required for both NO and NO_2. The reference standard for the calibration may be either an NO or NO_2 standard. The reference standard must be used to certify the other standard to ensure consistency between the two standards.

2.3.1.1 *NO_2 concentration standard.* A permeation device suitable for generating NO_2 concentrations at the required flowrates over the required concentration range. If the permeation device is used as the reference standard, it must be traceable to a National Bureau of Standards NO_2 Standard Reference Material (SRM 1629) or NO in N_2 Standard Reference Material (SRM 1683 or SRM 1684). If an NO cylinder is used as the reference standard, the NO_2 permeation device must be certified against the NO standard according to the procedure given in reference 13. The use of the permeation device should be in strict accordance with the instructions supplied with the device. Additional information regarding the use of permeation devices is given by Scaringelli et al. (*11*) and Rook et al. (*12*).

2.3.1.2 *NO concentration standard.* Cylinder containing 50 to 100 ppm NO in N_2 with less than 1 ppm NO_2. If the cylinder is used as the reference standard, it must be traceable to a National Bureau of Standards NO in N_2 Standard Reference Material (SRM 1683 or SRM 1684) or NO_2 Standard Reference Material (SRM 1629). If an NO_2 permeation device is used as the reference standard, the NO cylinder must be certified against the NO_2 standard according to the procedure given in reference 13. The cylinder should be recertified on a regular basis as determined by the local quality control program. A procedure for determining the amount of NO_2 impurity in the NO cylinder is also given in reference 13.

2.3.3 *Zero air.* Air, free of contaminants which might react with NO or NO_2 or cause a detectable response on the $NO/NO_x/NO_2$ analyzer. When using permeation devices that are sensitive to moisture, the zero air passing across the permeation device must be dry to avoid surface reactions on the device. (Refer to the supplier's instructions for use of the permeation device.) A procedure for generating zero air is given in reference 13.

2.4 *Procedure.*

2.4.1 Assemble the calibration apparatus such as the typical one shown in Figure 2.

2.4.2 Insure that all flowmeters are calibrated under the conditions of use against a reliable standard such as a soap bubble meter or wet-test meter. All volumetric flowrates should be corrected to 25° C and 760 mm Hg. A discussion on the calibration of flowmeters is given in reference 13.

2.4.3 Install the permeation device in the constant temperature chamber. Provide a small fixed air flow (200-400 scm³/min) across the device. The permeation device should always have a continuous air flow across it to prevent large buildup of NO_2 in the system and a consequent restabilization period. Record the flowrate as FP. Allow the device to stabilize at the calibration temperature for at least 24 hours. The temperature must be adjusted and controlled to within ±0.1 °C or less of the calibration temperature as monitored with the temperature measuring device.

2.4.4 Precautions must be taken to remove O_2 and other contaminants from the NO pressure regulator and delivery system prior to the start of calibration to avoid any conversion of the standard NO to NO_2. Failure to do so can cause significant errors in calibration. This problem may be minimized by (1) Carefully evacuating the regulator, when possible, after the regulator has been connected to the cylinder and before opening the cylinder valve; (2) Thoroughly flushing the regulator and delivery system with NO after opening the cylinder valve; (3) Not removing the regulator from the cylinder between calibrations unless absolutely necessary. Further discussion of these procedures is given in reference 13.

2.4.5 Select the operating range of the NO/NO_x/NO_2 analyzer to be calibrated. In order to obtain maximum precision and accuracy for NO_2 calibration, all three channels of the analyzer should be set to the same range. If operation of the NO and NO_x channels on higher ranges is desired, subsequent recalibration of the NO and NO_x channels on the higher ranges is recommended.

NOTE.—Some analyzer designs may require identical ranges for NO, NO_x, and NO_2 during operation of the analyzer.

2.4.6 Connect the recorder output cable(s) of the NO/NO_x/NO_2 analyzer to the input terminals of the strip chart recorder(s). All adjustments to the analyzer should be performed based on the appropriate strip chart readings. References to analyzer responses in the procedures given below refer to recorder responses.

2.4.7 Switch the valve to vent the flow from the permeation device and adjust the diluent air flowrate, F_D, to provide zero air at the output manifold. The total air flow must exceed the total demand of the analyzer(s) connected to the output manifold to insure that no ambient air is pulled into the manifold vent. Allow the analyzer to sample zero air until stable NO, NO_x, and NO_2 responses are obtained. After the responses have stabilized, adjust the analyzer zero control(s).

NOTE.—Some analyzers may have separate zero controls for NO, NO_x, and NO_2. Other analyzers may have separate zero controls only for NO and NO_x, while still others may have only one zero common control to all three channels.

Offsetting the analyzer zero adjustments to +5% of scale is recommended to facilitate observing negative zero drift. Record the stable zero air responses as Z_{NO}, Z_{NO_x}, and Z_{NO_2}.

2.4.8 Preparation of NO and NO_x calibration curves.

2.4.8.1 Adjustment of NO span control. Adjust the NO flow from the standard NO cylinder to generate an NO concentration of approximately 80% of the upper range limit (URL) of the NO range. The exact NO concentration is calculated from:

$$[NO]_{OUT}=\frac{F_{NO}\times[NO]_{STD}}{F_{NO}+F_D}\qquad(16)$$

where:

$[NO]_{OUT}$ = diluted NO concentration at the output manifold, ppm

F_{NO} = NO flowrate, scm³/min

$[NO]_{STD}$ = concentration of the undiluted NO standard, ppm

F_D = diluent air flowrate, scm³/min

Sample this NO concentration until the NO and NO_x responses have stabilized. Adjust the NO span control to obtain a recorder response as indicated below:

recorder response (% scale)

$$=\left(\frac{[NO]_{OUT}}{URL}\times100\right)+Z_{NO}\qquad(17)$$

where:

URL = nominal upper range limit of the NO channel, ppm

NOTE.—Some analyzers may have separate span controls for NO, NO_x, and NO_2. Other analyzers may have separate span controls only for NO and NO_x, while still others may have only one span control common to all three channels. When only one span control is available, the span adjustment is made on the NO channel of the analyzer.

If substantial adjustment of the NO span control is necessary, it may be necessary to recheck the zero and span adjustments by repeating steps 2.4.7 and 2.4.8.1. Record the NO concentration and the analyzer's NO response.

2.4.8.2 *Adjustment of NO_x span control.* When adjusting the analyzer's NO_x span control, the presence of any NO_2 impurity in the standard NO cylinder must be taken into account. Procedures for determining the amount of NO_2 impurity in the standard NO cylinder are given in reference 13. The exact NO_x concentration is calculated from:

$$[NO_x]_{OUT}=\frac{F_{NO}\times([NO]_{STD}+[NO_2]_{IMP})}{F_{NO}+F_D}\qquad(18)$$

where:

$[NO_x]_{OUT}$ = diluted NO_x concentration at the output manifold, ppm

$[NO_2]_{IMP}$ = concentration of NO_2 impurity in the standard NO cylinder, ppm

Adjust the NO_x span control to obtain a convenient recorder response as indicated below:

recorder response (% scale)

$$=\left(\frac{[NO_x]_{OUT}}{URL}\times100\right)+Z_{NO_x}\qquad(19)$$

NOTE: If the analyzer has only one span control, the span adjustment is made on the NO channel and no further adjustment is made here for NO_x.

If substantial adjustment of the NO_x span control is necessary, it may be necessary to recheck the zero and span adjustments by repeating steps 2.4.7 and 2.4.8.2. Record the NO_x concentration and the analyzer's NO_x response.

2.4.8.3 Generate several additional concentrations (at least five evenly spaced points across the remaining scale are suggested to verify linearity) by decreasing F_{NO} or increasing F_D. For each concentration generated, calculate the exact NO and NO_x concentrations using equations (16) and (18) respectively. Record the analyzer's NO and NO_x responses for each concentration. Plot the analyzer responses versus the respective calculated NO and NO_x concentrations and draw or calculate the NO and NO_x calibration curves. For subsequent calibrations where linearity can be assumed, these curves may be checked with a two-point calibration consisting of a zero point and NO and NO_x concentrations of approximately 80 percent of the URL.

2.4.9 Preparation of NO_2 calibration curve.

2.4.9.1 Remove the NO flow. Assuming the NO_2 zero has been properly adjusted while sampling zero air in step 2.4.7, switch the valve to provide NO_2 at the output manifold.

2.4.9.2 Adjust F_D to generate an NO_2 concentration of approximately 80 percent of the *URL* of the NO_2 range. The total air flow must exceed the demand of the analyzer(s) under calibration. The actual concentration of NO_2 is calculated from:

$$[NO_2]_{OUT}=\frac{R\times K}{F_P+F_D}\qquad(20)$$

where:

$[NO_2]_{OUT}$ = diluted NO_2 concentration at the output manifold, ppm

R = permeation rate, µg/min

K = 0.532 µl NO_2/µg NO_2 (at 25 °C and 760 mm Hg)

F_P = air flowrate across permeation device, scm³/min

F_D = diluent air flowrate, scm³/min

Sample this NO_2 concentration until the NO_x and NO_2 responses have stabilized. Adjust the NO_2 span control to obtain a recorder response as indicated below:

recorder response (percent scale)

$$=\left(\frac{[NO_2]_{OUT}}{URL}\times100\right)+Z_{NO_2}\qquad(21)$$

NOTE: If the analyzer has only one or two span controls, the span adjustments are made on the NO channel or NO and NO_x channels and no further adjustment is made here for NO_2.

If substantial adjustment of the NO_2 span control is necessary it may be necessary to recheck the zero and span adjustments by repeating steps 2.4.7 and 2.4.9.2. Record the NO_2 concentration and the analyzer's NO_2 response. Using the NO_x calibration curve obtained in step 2.4.8, measure and record the NO_x concentration as $[NO_x]_M$.

2.4.9.3 Adjust F_D to obtain several other concentrations of NO_2 over the NO_2 range (at least five evenly spaced points across the remaining scale are suggested). Calculate each NO_2 concentration using equation (20) and record the corresponding analyzer NO_x and NO_2 responses. Plot the analyzer's NO_2 responses versus the corresponding calculated NO_2 concentrations and draw or calculate the NO_2 calibration curve.

2.4.10 *Determination of converter efficiency.*

2.4.10.1 Plot $[NO_x]_M$ (y-axis) versus $[NO_2]_{OUT}$ (x-axis) and draw or calculate the converter efficiency curve. The slope of the curve times 100 is the average converter efficiency, E_c. The average converter efficiency must be greater than 96 percent; if it is less than 96 percent, replace or service the converter.

NOTE. Supplemental information on calibration and other procedures in this method are given in reference 13.

3. *Frequency of calibration.* The frequency of calibration, as well as the number of points necessary to establish the calibration curve and the frequency of other performance checks, will vary from one analyzer to another. The user's quality control program should provide guidelines for initial establishment of these variables and for subsequent alteration as operational experience is accumulated. Manufacturers of analyzers should include in their instruction/operation manuals information and guidance as to these variables and on other matters of operation, calibration, and quality control.

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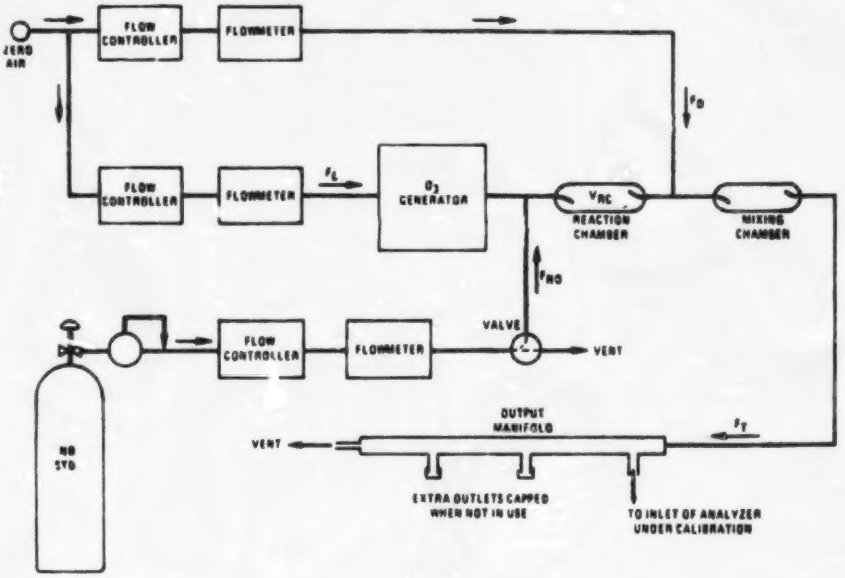
ZERO AIR
FLOW CONTROLLER
FLOWMETER
F_D
FLOW CONTROLLER
FLOWMETER
F_O
O_3 GENERATOR
V_{RC}
REACTION CHAMBER
MIXING CHAMBER
F_{NO}
VALVE
FLOW CONTROLLER
FLOWMETER
VENT
NO STD
OUTPUT MANIFOLD
F_T
VENT
EXTRA OUTLETS CAPPED WHEN NOT IN USE
TO INLET OF ANALYZER UNDER CALIBRATION

Figure 1. Schematic diagram of a typical GPT calibration system.

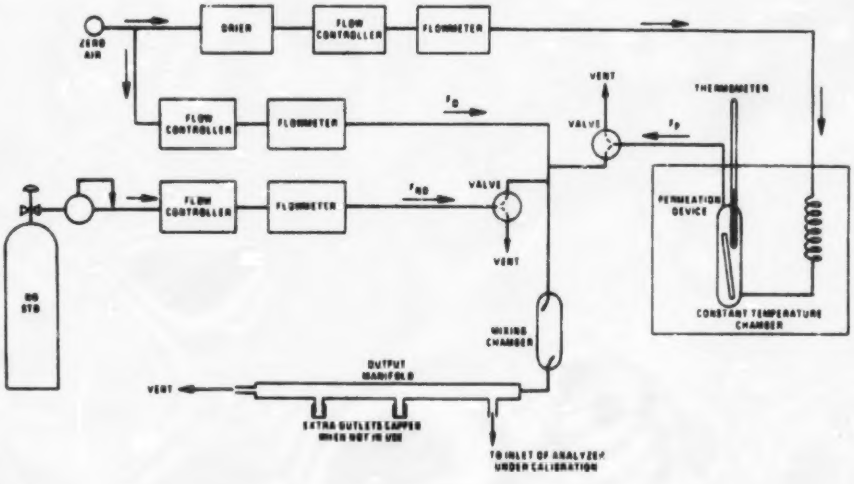
ZERO AIR
DRIER
FLOW CONTROLLER
FLOWMETER
FLOW CONTROLLER
FLOWMETER
F_D
VENT
THERMOMETER
VALVE
F_P
FLOW CONTROLLER
FLOWMETER
F_{NO}
VALVE
VENT
PERMEATION DEVICE
NO STD
MIXING CHAMBER
CONSTANT TEMPERATURE CHAMBER
OUTPUT MANIFOLD
VENT
EXTRA OUTLETS CAPPED WHEN NOT IN USE
TO INLET OF ANALYZER UNDER CALIBRATION

Figure 2. Schematic diagram of a typical calibration apparatus using an NO_2 permeation device

(Sec. 4, Pub. L. 91-604, 84 Stat. 1678 (42 U.S.C. 1857c-4))

[41 FR 52688, Dec. 1, 1976]

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Appendix G

APPENDIX G—REFERENCE METHOD FOR THE DETERMINATION OF LEAD IN SUSPENDED PARTICULATE MATTER COLLECTED FROM AMBIENT AIR

1. *Principle and applicability.*

1.1 Ambient air suspended particulate matter is collected on a glass-fiber filter for 24 hours using a high volume air sampler.

1.2 Lead in the particulate matter is solubilized by extraction with nitric acid (HNO_3), facilitated by heat or by a mixture of HNO_3 and hydrochloric acid (HCl) facilitated by ultrasonication.

1.3 The lead content of the sample is analyzed by atomic absorption spectrometry using an air-acetylene flame, the 283.3 or 217.0 nm lead absorption line, and the optimum instrumental conditions recommended by the manufacturer.

1.4 The ultrasonication extraction with HNO_3/HCl will extract metals other than lead from ambient particulate matter.

2. *Range, sensitivity, and lower detectable limit.* The values given below are typical of the methods capabilities. Absolute values will vary for individual situations depending on the type of instrument used, the lead line, and operating conditions.

2.1 *Range.* The typical range of the method is 0.07 to 7.5 μg Pb/m^3 assuming an upper linear range of analysis of 15 μg/ml and an air volume of 2,400 m^3.

2.2 *Sensitivity.* Typical sensitivities for a 1 percent change in absorption (0.0044 absorbance units) are 0.2 and 0.5 μg Pb/ml for the 217.0 and 283.3 nm lines, respectively.

2.3 *Lower detectable limit (LDL).* A typical LDL is 0.07 μg Pb/m^3. The above value was calculated by doubling the between-laboratory standard deviation obtained for the lowest measurable lead concentration in a collaborative test of the method.(*15*) An air volume of 2,400 m^3 was assumed.

3. *Interferences.* Two types of interferences are possible: chemical and light scattering.

3.1 *Chemical.* Reports on the absence (*1, 2, 3, 4, 5*) of chemical interferences far outweigh those reporting their presence, (*6*) therefore, no correction for chemical interferences is given here. If the analyst suspects that the sample matrix is causing a chemical interference, the interference can be verified and corrected for by carrying out the analysis with and without the method of standard additions.(*7*)

3.2 *Light scattering.* Nonatomic absorption or light scattering, produced by high concentrations of dissolved solids in the sample, can produce a significant interference, especially at low lead concentrations. (*2*) The interference is greater at the 217.0 nm line than at the 283.3 nm line. No interference was observed using the 283.3 nm line with a similar method.(*1*)

Light scattering interferences can, however, be corrected for instrumentally. Since the dissolved solids can vary depending on the origin of the sample, the correction may be necessary, especially when using the 217.0 nm line. Dual beam instruments with a continuum source give the most accurate correction. A less accurate correction can be obtained by using a nonabsorbing lead line that is near the lead analytical line. Information on use of these correction techniques can be obtained from instrument manufacturers' manuals.

If instrumental correction is not feasible, the interference can be eliminated by use of the ammonium pyrrolidinecarbodithioate-methylisobutyl ketone, chelation-solvent extraction technique of sample preparation.(*8*)

4. *Precision and bias.*

4.1 The high-volume sampling procedure used to collect ambient air particulate matter has a between-laboratory relative standard deviation of 3.7 percent over the range 80 to 125 μg/m^3.(*9*) The combined extraction-analysis procedure has an average within-laboratory relative standard deviation of 5 to 6 percent over the range 1.5 to 15 μg Pb/ml, and an average between laboratory relative standard deviation of 7 to 9 percent over the same range. These values include use of either extraction procedure.

4.2 Single laboratory experiments and collaborative testing indicate that there is no significant difference in lead recovery between the hot and ultrasonic extraction procedures.(*15*)

5. *Apparatus.*

5.1 *Sampling.*

5.1.1 *High-volume sampler.* Use and calibrate the sampler as described in reference 10.

5.2 *Analysis.*

5.2.1 *Atomic absorption spectrophotometer.* Equipped with lead hollow cathode or electrodeless discharge lamp.

5.2.1.1 *Acetylene.* The grade recommended by the instrument manufacturer should be used. Change cylinder when pressure drops below 50-100 psig.

5.2.1.2 *Air.* Filtered to remove particulate, oil, and water.

5.2.2 *Glassware.* Class A borosilicate glassware should be used throughout the analysis.

5.2.2.1 *Beakers.* 30 and 150 ml. graduated, Pyrex.

5.2.2.2 *Volumetric flasks.* 100-ml.

5.2.2.3 *Pipettes.* To deliver 50, 30, 15, 8, 4, 2, 1 ml.

5.2.2.4 *Cleaning.* All glassware should be scrupulously cleaned. The following procedure is suggested. Wash with laboratory detergent, rinse, soak for 4 hours in 20 percent (w/w) HNO_3, rinse 3 times with distilled-deionized water, and dry in a dust free manner.

5.2.3 *Hot plate.*

5.2.4 *Ultrasonication water bath, unheated.* Commercially available laboratory ultrasonic cleaning baths of 450 watts or higher "cleaning power," i.e., actual ultrasonic power output to the bath have been found satisfactory.

5.2.5 *Template.* To aid in sectioning the glass-fiber filter. See figure 1 for dimensions.

5.2.6 *Pizza cutter.* Thin wheel. Thickness 1mm.

5.2.7 *Watch glass.*

5.2.8 *Polyethylene bottles.* For storage of samples. Linear polyethylene gives better storage stability than other polyethylenes and is preferred.

5.2.9 Parafilm "M".[*] American Can Co., Marathon Products, Nennah, Wis., or equivalent.

6. *Reagents.*

6.1 *Sampling.*

6.1.1 *Glass fiber filters.* The specifications given below are intended to aid the user in obtaining high quality filters with reproducible properties. These specifications have been met by EPA contractors.

6.1.1.1 *Lead content.* The absolute lead content of filters is not critical, but low values are, of course, desirable. EPA typically obtains filters with a lead content of 75 μg/filter.

It is important that the variation in lead content from filter to filter, within a given batch, be small.

6.1.1.2 *Testing.*

6.1.1.2.1 For large batches of filters (>500 filters) select at random 20 to 30 filters from a given batch. For small batches (<500 filters) a lesser number of filters may be taken. Cut one ¾"x8" strip from each filter anywhere in the filter. Analyze all strips, separately, according to the directions in sections 7 and 8.

6.1.1.2.2 Calculate the total lead in each filter as

$$F_b = \mu\text{g Pb/ml} \times \frac{100\ \text{ml}}{\text{strip}} \times \frac{12\ \text{strips}}{\text{filter}}$$

where:

F_b = Amount of lead per 72 square inches of filter, μg.

6.1.1.2.3 Calculate the mean, F_b, of the values and the relative standard deviation (standard deviation/mean × 100). If the relative standard deviation is high enough so that, in the analysts opinion, subtraction of F_b, (section 10.3) may result in a significant error in the μg Pb/m^3 the batch should be rejected.

6.1.1.2.4 For acceptable batches, use the value of F_b to correct all lead analyses (section 10.3) of particulate matter collected using that batch of filters. If the analyses are below the LDL (section 2.3) no correction is necessary.

6.2 *Analysis.*

6.2.1 Concentrated (15.6 *M*) HNO_3. ACS reagent grade HNO_3 and commercially available redistilled HNO_3 has found to have sufficiently low lead concentrations.

6.2.2 Concentrated (11.7 *M*) HCl. ACS reagent grade.

6.2.3 *Distilled-deionized water.* (D.I. water).

6.2.4 3 *M* HNO_3. This solution is used in the hot extraction procedure. To prepare, add 192 ml of concentrated HNO_3 to D.I. water in a 1 *l* volumetric flask. Shake well, cool, and dilute to volume with D.I. water. *Caution:* Nitric acid fumes are toxic. Prepare in a well ventilated fume hood.

6.2.5 0.45 *M* HNO_3. This solution is used as the matrix for calibration standards when using the hot extraction procedure. To prepare, add 29 ml of concentrated HNO_3 to D.I. water in a 1 *l* volumetric flask. Shake well, cool, and dilute to volume with D.I. water.

6.2.6 2.6 *M* HNO_3 + 0 to 0.9 *M* HCl. This solution is used in the ultrasonic extraction procedure. The concentration of HCl can be varied from 0 to 0.9 *M*. Directions are given for preparation of a 2.6 *M* HNO_3 + 0.9 *M* HCl solution. Place 167 ml of concentrated HNO_3 into a 1 *l* volumetric flask and add 77 ml of concentrated HCl. Stir 4 to 6 hours, dilute to nearly 1 *l* with D.I. water, cool to room temperature, and dilute to 1 *l*.

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[*] Mention of commercial products does not imply endorsement by the U.S. Environmental Protection Agency.

6.2.7 0.40 *M* HNO_3 + X *M* HCl. This solution is used as the matrix for calibration standards when using the ultrasonic extraction procedure. To prepare, add 26 ml of concentrated HNO_3 plus the ml of HCl required, to a 1 *l* volumetric flask. Dilute to nearly 1 *l* with D.I. water, cool to room temperature, and dilute to 1 *l*. The amount of HCl required can be determined from the following equation:

$$y = \frac{77 \text{ ml} \times 0.15 \times}{0.9 \text{ M}}$$

where:

y = ml of concentrated HCl required.
x = molarity of HCl in 6.2.6.
0.15 = dilution factor in 7.2.2.

6.2.8 Lead nitrate, $Pb(NO_3)_2$, ACS reagent grade, purity 99.0 percent. Heat for 4 hours at 120 °C and cool in a desiccator.

6.3 *Calibration standards.*

6.3.1 Master standard, 1000 μg Pb/ml in HNO_3. Dissolve 1.598 g of $Pb(NO_3)_2$ in 0.45 *M* HNO_3 contained in a 1 *l* volumetric flask and dilute to volume with 0.45 *M* HNO_3.

6.3.2 Master standard, 1000 μg Pb/ml in HNO_3/HCl. Prepare as in 6.3.1 except use the HNO_3/HCl solution in 6.2.7.

Store standards in a polyethylene bottle. Commercially available certified lead standard solutions may also be used.

7. *Procedure.*

7.1 *Sampling.* Collect samples for 24 hours using the procedure described in reference *10* with glass-fiber filters meeting the specifications in 6.1.1. Transport collected samples to the laboratory taking care to minimize contamination and loss of sample (*16*).

7.2 *Sample preparation.*

7.2.1 *Hot extraction procedure.*

7.2.1.1 Cut a ¾" x 8" strip from the exposed filter using a template and a pizza cutter as described in Figures 1 and 2. Other cutting procedures may be used.

Lead in ambient particulate matter collected on glass fiber filters has been shown to be uniformly distributed across the filter.[1, 3, 11] Another study [12] has shown that when sampling near a roadway, strip position contributes significantly to the overall variability associated with lead analyses. Therefore, when sampling near a roadway, additional strips should be analyzed to minimize this variability.

7.2.1.2 Fold the strip in half twice and place in a 150-ml beaker. Add 15 ml of 3 *M* HNO_3 to cover the sample. The acid should completely cover the sample. Cover the beaker with a watch glass.

7.2.1.3 Place beaker on the hot-plate, contained in a fume hood, and boil gently for 30 min. Do not let the sample evaporate to dryness. *Caution:* Nitric acid fumes are toxic.

7.2.1.4 Remove beaker from hot plate and cool to near room temperature.

7.2.1.5 Quantitatively transfer the sample as follows:

7.2.1.5.1 Rinse watch glass and sides of beaker with D.I. water.

7.2.1.5.2 Decant extract and rinsings into a 100-ml volumetric flask.

7.2.1.5.3 Add D.I. water to 40 ml mark on beaker, cover with watch glass, and set aside for a minimum of 30 minutes. This is a critical step and cannot be omitted since it allows the HNO_3 trapped in the filter to diffuse into the rinse water.

7.2.1.5.4 Decant the water from the filter into the volumetric flask.

7.2.1.5.5 Rinse filter and beaker twice with D.I. water and add rinsings to volumetric flask until total volume is 80 to 85 ml.

7.2.1.5.6 Stopper flask and shake vigorously. Set aside for approximately 5 minutes or until foam has dissipated.

7.2.1.5.7 Bring solution to volume with D.I. water. Mix thoroughly.

7.2.1.5.8 Allow solution to settle for one hour before proceeding with analysis.

7.2.1.5.9 If sample is to be stored for subsequent analysis, transfer to a linear polyethylene bottle.

7.2.2 *Ultrasonic extraction procedure.*

7.2.2.1 Cut a ¾" x 8" strip from the exposed filter as described in section 7.2.1.1.

7.2.2.2 Fold the strip in half twice and place in a 30 ml beaker. Add 15 ml of the HNO_3/HCl solution in 6.2.6. The acid should completely cover the sample. Cover the beaker with parafilm.

The parafilm should be placed over the beaker such that none of the parafilm is in contact with water in the ultrasonic bath. Otherwise, rinsing of the parafilm (section 7.2.2.4.1) may contaminate the sample.

7.2.2.3 Place the beaker in the ultrasonication bath and operate for 30 minutes.

7.2.2.4 Quantitatively transfer the sample as follows:

7.2.2.4.1 Rinse parafilm and sides of beaker with D.I. water.

7.2.2.4.2 Decant extract and rinsings into a 100 ml volumetric flask.

7.2.2.4.3 Add 20 ml D.I. water to cover the filter strip, cover with parafilm, and set aside for a minimum of 30 minutes. This is a critical step and cannot be omitted. The sample is then processed as in sections 7.2.1.5.4 through 7.2.1.5.9.

NOTE: Samples prepared by the hot extraction procedure are now in 0.45 *M* HNO_3. Samples prepared by the ultrasonication procedure are in 0.40 *M* HNO_3 + X *M* HCl.

8. *Analysis.*

8.1 Set the wavelength of the monochromator at 283.3 or 217.0 nm. Set or align other instrumental operating conditions as recommended by the manufacturer.

8.2 The sample can be analyzed directly from the volumetric flask, or an appropriate amount of sample decanted into a sample analysis tube. In either case, care should be taken not to disturb the settled solids.

8.3 Aspirate samples, calibration standards and blanks (section 9.2) into the flame and record the equilibrium absorbance.

8.4 Determine the lead concentration in μg Pb/ml, from the calibration curve, section 9.3.

8.5 Samples that exceed the linear calibration range should be diluted with acid of the same concentration as the calibration standards and reanalyzed.

9. *Calibration.*

9.1 Working standard, 20 μg Pb/ml. Prepared by diluting 2.0 ml of the master standard (6.3.1 if the hot acid extraction was used or 6.3.2 if the ultrasonic extraction procedure was used) to 100 ml with acid of the same concentration as used in preparing the master standard.

9.2 *Calibration standards.* Prepare daily by diluting the working standard, with the same acid matrix, as indicated below. Other lead concentrations may be used.

Volume of 20 μg/ml working standard, ml	Final volume, ml	Concentration μg Pb/ml
0	100	0
1.0	200	0.1
2.0	200	0.2
2.0	100	0.4
4.0	100	0.8
8.0	100	1.6
15.0	100	3.0
30.0	100	6.0
50.0	100	10.0
100.0	100	20.0

9.3 *Preparation of calibration curve.* Since the working range of analysis will vary depending on which lead line is used and the type of instrument, no one set of instructions for preparation of a calibration curve can be given. Select standards (plus the reagent blank), in the same acid concentration as the samples, to cover the linear absorption range indicated by the instrument manufacturer. Measure the absorbance of the blank and standards as in section 8.0. Repeat until good agreement is obtained between replicates. Plot absorbance (y-axis) versus concentration in μg Pb/ml (x-axis). Draw (or compute) a straight line through the linear portion of the curve. Do not force the calibration curve through zero. Other calibration procedures may be used.

To determine stability of the calibration curve, remeasure—alternately—one of the following calibration standards for every 10th sample analyzed: Concentration ≤ 1μg Pb/ml; concentration ≤ 10 μg Pb/ml. If either standard deviates by more than 5 percent from the value predicted by the calibration curve, recalibrate and repeat the previous 10 analyses.

10. *Calculation.*

10.1 *Measured air volume.* Calculate the measured air volume at Standard Temperature and Pressure as described in Reference 10.

10.2 *Lead concentration.* Calculate lead concentration in the air sample.

$$C = \frac{(\mu g \text{ Pb/ml} \times 100 \text{ ml/strip} \times 12 \text{ strips/filter}) - F_b}{V_{STP}}$$

where:

C = Concentration, μg Pb/sm³.
μg Pb/ml = Lead concentration determined from section 8.
100 ml/strip = Total sample volume.
12 strips = Total useable filter area, 8" × 9". Exposed area of one strip, ¾" × 7".
Filter = Total area of one strip, ¾" × 8".
F_b = Lead concentration of blank filter, μg, from section 6.1.1.2.3.
V_{STP} = Air volume from 10.2.

11. *Quality control.*

¾" × 8" glass fiber filter strips containing 80 to 2000 μg Pb/strip (as lead salts) and blank strips with zero Pb content should be used to determine if the method—as being used—has any bias. Quality control charts should be established to monitor differences between measured and true values. The frequency of such checks will depend on the local quality control program.

To minimize the possibility of generating unreliable data, the user should follow practices established for assuring the quality of air pollution data, (*13*) and take part in EPA's semiannual audit program for lead analyses.

12. *Trouble shooting.*

1. During extraction of lead by the hot extraction procedure, it is important to keep the sample covered so that corrosion products—formed on fume hood surfaces which may contain lead—are not deposited in the extract.

2. The sample acid concentration should minimize corrosion of the nebulizer. However, different nebulizers may require lower acid concentrations. Lower concentrations can be used provided samples and standards have the same acid concentration.

3. Ashing of particulate samples has been found, by EPA and contractor laboratories, to be unnecessary in lead analyses by atomic absorption. Therefore, this step was omitted from the method.

4. Filtration of extracted samples, to remove particulate matter, was specifically excluded from sample preparation, because some analysts have observed losses of lead due to filtration.

5. If suspended solids should clog the nebulizer during analysis of samples, centrifuge the sample to remove the solids.

13. *Authority.*

(Secs. 109 and 301(a), Clean Air Act as amended. (42 U.S.C. 7409, 7601(a)).)

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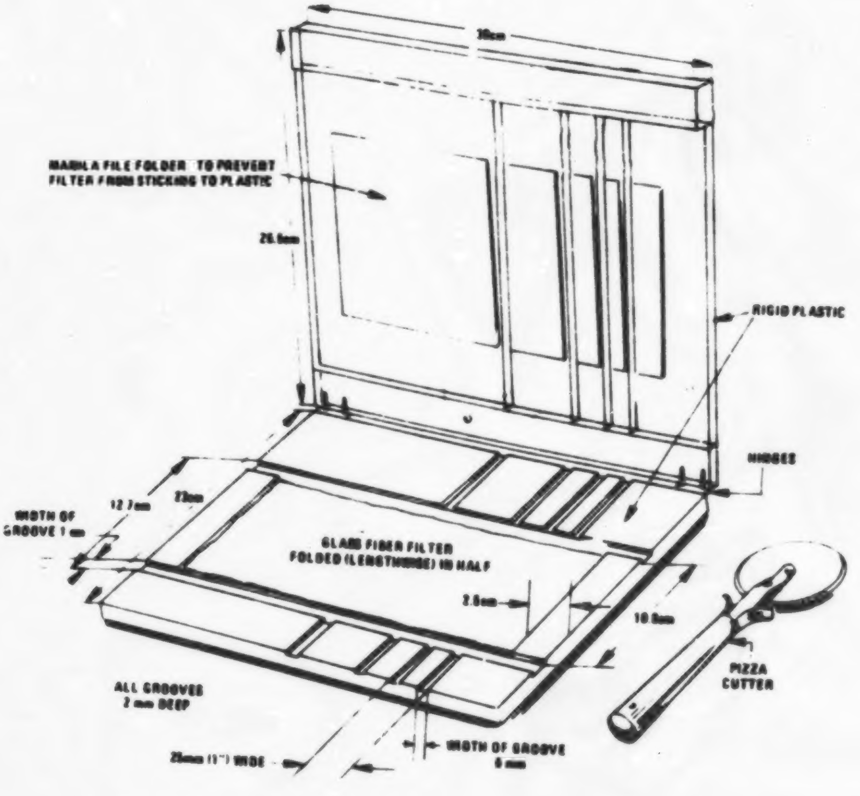

Figure 1

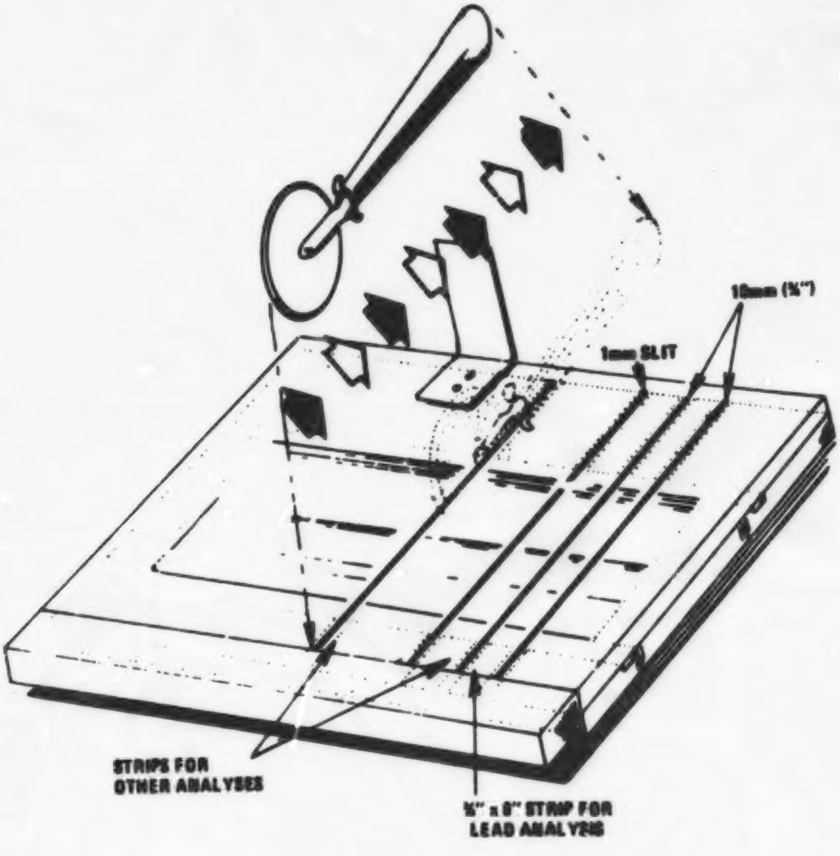
19mm (¾")
1mm SLIT
STRIPS FOR OTHER ANALYSES
¾" x 8" STRIP FOR LEAD ANALYSIS

Figure 2

(Secs. 109, 301(a) of the Clean Air Act, as amended (42 U.S.C. 7409, 7601(a))
[43 FR 46258, Oct. 5, 1978, as amended at 44 FR 37915, June 29, 1979]

Appendix 3

Conversion Factors and Useful Information

International Metric System — Le Systeme International d’Unites (SI Units)

Base Units of the International Metric System (SI)		
Quantity	**Name of the Unit**	**Symbol**
Length	meter	m
Mass	kilogram	kg
Time	second	s
Temperature	Kelvin	K
Electric current	ampere	A
Luminous intensity	candela	cd
Amount of substance	mole	mol

Recommended decimal multiples and submultiples and the corresponding prefixes and names.

Factor	Prefix	Symbol	Meaning
10^{12}	tera	T	One trillion times
10^{9}	giga	G	One billion times
10^{6}	mega	M	One million times
10^{3}	kilo	k	One thousand times
10^{2}	hecto	h	One hundred times
10	deca	da	Ten times
10^{-1}	deci	d	One tenth of
10^{-2}	centi	c	One hundredth of
10^{-3}	milli	m	One thousandth of
10^{-6}	micro	μ	One millionth of
10^{-9}	nano	n	One billionth of
10^{-12}	pico	p	One trillionth of
10^{-15}	femto	f	One quadrillionth of
10^{-18}	atto	a	One quintillionth of

Pressure

From \ To	mmHg	in Hg	In H_2O	ft H_2O	atm	lb/in^2	Kg/cm^2
mm Hg	1	0.03937	0.5353	0.04460	0.00132	0.01934	0.00136
in Hg	25.40	1	13.60	1.133	0.03342	0.4912	0.03453
In H_2O	1.868	0.07355	1	0.08333	0.00246	0.03613	0.00254
ft H_2O	22.42	0.8826	12	1	0.02950	0.4335	0.03048
atm	760	29.92	406.8	33.90	1	14.70	1.033
lb/in^2	51.71	2.036	27.67	2.307	0.06805	1	0.07031
Kg/cm^2	735.6	28.96	393.7	32.81	0.9678	14.22	1

Volume

From \ To	cm³	liter	m³	in³	ft³
cm³	1	0.001	1×10^{-6}	0.06102	3.53×10^{-5}
liter	1000	1	0.001	61.02	0.03532
m³	1×10^{-6}	1000	1	6.10×10^{-4}	35.31
in³	16.39	0.01639	1.64×10^{-6}	1	5.79×10^{-4}
ft³	2.83×10^{-4}	28.32	0.02832	1728	1

Temperature

°C = 5/9 (°F − 32)	°F = 9/5 °C + 32
°K = °C + 273.2	°R = °F + 459.7

Conversion factors — flow

Given units \ Desired units	M³/sec	M³/min	M³/hour	ft³/sec	ft³/min	ft³/hour	L/sec	L/min	cm³/sec	cm³/min
M³/sec	1	60	3600	35.3144	21.1887×10^{2}	12.7132×10^{4}	999.973	59.998×10^{3}	1×10^{6}	6×10^{7}
M³/min	0.0167	1	60	0.5886	35.3144	21.189×10^{2}	16.667	999.973	16.667×10^{3}	1×10^{6}
M³/hour	2.778×10^{-5}	16.667×10^{-3}	1	98.90×10^{-4}	0.5886	35.3144	27.777×10^{-2}	16.667	2.777×10^{2}	1.666×10^{4}
ft³/sec	28.317×10^{-3}	1.699	101.94	1	60	3600	28.316	16.9896×10^{2}	2.8317×10^{4}	1.699×10^{6}
ft³/min	4.7195×10^{-4}	28.317×10^{-3}	1.699	16.667×10^{-3}	1	60	47.193×10^{-2}	28.316	4.7195×10^{2}	2.8317
ft³/hour	7.8658×10^{-6}	4.7195×10^{-4}	28.317×10^{-3}	2.778×10^{-4}	16.667×10^{-3}	1	7.866×10^{-3}	0.4719	78.658	4.7195×10^{2}
L/sec	1.000027×10^{-3}	6.00016×10^{-2}	3.6	35.316×10^{-3}	2.11896	127.138	1	60	1000.027	16.667
L/min	1.6667×10^{-5}	1.000027×10^{-3}	6.00016×10^{-2}	5.886×10^{-4}	35.316×10^{-3}	2.11896	1.6667×10^{-2}	1	16.6667	1000.027
cm³/sec	1×10^{-6}	6×10^{-5}	3.6×10^{-3}	3.5314×10^{-5}	2.1189×10^{-3}	1.271×10^{-3}	9.99973×10^{-4}	5.9998×10^{-2}	1	16.667×10^{-3}
cm³/min	1.6667×10^{-8}	1×10^{-6}	6×10^{-5}	5.886×10^{-7}	0.3531×10^{-4}	2.11887×10^{-3}	5.9998×10^{-2}	9.99973×10^{-4}	60	1

To convert a value from a given unit to a desired unit, multiply the given value by the factor opposite the given unit and beneath the desired unit.

Conversion factors—ppm vs. **μg/m³**

Desired unit / Given unit	Parts per million by volume—ppm					
	O_3	NO_2	SO_2	H_2S	CO	HC as methane
μg/m³	5.10×10^{-4}	5.32×10^{-4}	3.83×10^{-4}	7.19×10^{-4}	—	—
mg/m³	—	—	—	—	0.875	1.53

Desired unit / Given unit	μg/m³				mg/m³	
	O_3	NO_2	SO_2	H_2S	CO	HC
ppm	1960	1880	2610	1390	1.14	0.654

To convert a value from a given unit to a desired unit, multiply the given value by the factor opposite the given units and beneath the desired unit.

Atomic weight and numbers

Name	Symbol	Atomic number	Atomic weight
Actinium	Ac	89	–
Aluminum	Al	13	26.9815
Americium	Am	95	–
Antimony	Sb	51	121.75
Argon	Ar	18	39.948
Arsenic	As	33	74.9216
Astatine	At	85	–
Barium	Ba	56	137.34
Berkelium	Bk	97	–
Beryllium	Be	4	9.0122
Bismuth	Bi	83	208.980
Boron	B	5	10.811
Bromine	Br	35	79.904
Cadmium	Cd	48	112.40
Calcium	Ca	20	40.08
Californium	Cf	98	–
Carbon	C	6	12.01115
Cerium	Ce	58	140.12
Cesium	Cs	55	132.905
Chlorine	Cl	17	35.453
Chromium	Cr	24	51.996
Cobalt	Co	27	58.9332
Copper	Cu	29	63.546
Curium	Cm	96	–
Dysprosium	Dy	66	162.50
Einsteinium	Es	99	–
Erbium	Er	68	167.26
Europium	Eu	63	151.96
Fermium	Fm	100	–
Fluorine	F	9	18.9984
Francium	Fr	87	–
Gadolinium	Gd	64	157.25
Gallium	Ga	31	69.72
Germanium	Ge	32	72.59
Gold	Au	79	196.967
Hafnium	Hf	72	178.49
Helium	He	2	4.0026
Holmium	Ho	67	164.930
Hydrogen	H	1	1.00797
Indium	In	49	114.82
Iodine	I	53	126.9044
Iridium	Ir	77	196.2
Iron	Fe	26	55.847
Krypton	Kr	36	83.80
Lanthanum	La	57	138.91
Lawrencium	Lr	103	–
Lead	Pb	82	207.19
Lithium	Li	3	6.939
Lutetium	Lu	71	174.97
Magnesium	Mg	12	24.312
Manganese	Mn	25	54.9380
Mendelevium	Md	101	–
Mercury	Hg	80	200.59
Molybdenum	Mo	42	95.94
Neodymium	Nd	60	144.24
Neon	Ne	10	20.183
Neptunium	Np	93	–
Nickel	Ni	28	58.71
Niobium	Nb	41	92.906
Nitrogen	N	7	14.0067
Nobelium	No	102	–
Osmium	Os	75	190.2
Oxygen	O	8	15.9994
Palladium	Pd	46	106.4
Phosphorus	P	15	30.9738
Platinum	Pt	78	195.09
Plutonium	Pu	94	–
Polonium	Po	84	–
Potassium	K	19	39.102
Praseodymium	Pr	59	140.907
Promethium	Pm	61	–
Protactinium	Pa	91	–
Radium	Ra	88	–
Radon	Rn	86	–
Rhenium	Re	75	186.2
Rhodium	Rh	45	102.905
Rubidium	Rb	37	84.57
Ruthenium	Ru	44	101.07
Samarium	Sm	62	150.35
Scandium	Sc	21	44.956
Selenium	Se	34	78.96
Silicon	Si	14	28.086
Silver	Ag	47	107.868
Sodium	Na	11	22.9898
Strontium	Sr	38	87.62
Sulfur	S	16	32.064
Tantalum	Ta	73	180.948
Technetium	Tc	43	–
Tellurium	Te	52	127.60
Terbium	Tb	65	158.924
Thallium	Tl	81	204.37
Thorium	Th	90	232.038
Thulium	Tm	59	168.934
Tin	Sn	50	118.69
Titanium	Ti	22	47.90
Tungsten	W	74	183.85
Uranium	V	92	238.03
Vanadium	V	23	50.942
Xenon	Xe	54	131.30
Ytterbium	Yb	70	173.04
Yttrium	Y	39	88.905
Zinc	Zn	30	65.37
Zirconium	Zr	40	91.22

Saturation vapor pressure over water (°C, mm Hg)[a]

Values for fractional degree between 50 and 89 were obtained by interpolation

Temp. °C	00	02	04	06	08
-15	1.436	1.414	1.390	1.368	1.345
-14	1.560	1.534	1.511	1.485	1.460
-13	1.691	1.665	1.637	1.611	1.585
-12	1.834	1.804	1.776	1.748	1.720
-11	1.987	1.955	1.924	1.893	1.863
-10	2.149	2.116	2.084	2.050	2.018
-9	2.326	2.289	2.254	2.219	2.184
-8	2.514	2.475	2.437	2.399	2.362
-7	2.715	2.674	2.633	2.593	2.553
-6	2.931	2.887	2.843	2.800	2.757
-5	3.163	3.115	3.069	3.022	2.976
-4	3.410	3.359	3.309	3.259	3.211
-3	3.673	3.620	3.567	3.514	3.461
-2	3.956	3.898	3.841	3.785	3.730
-1	4.258	4.196	4.135	4.075	4.016
-0	4.579	4.513	4.448	4.385	4.320
0	4.579	4.647	4.715	4.785	4.855
1	4.926	4.998	5.070	5.144	5.219
2	5.294	5.370	5.447	5.525	5.605
3	5.685	5.766	5.848	5.931	6.015
4	6.101	6.187	6.274	6.363	6.453
5	6.543	6.635	6.728	6.822	6.917
6	7.013	7.111	7.209	7.309	7.411
7	7.513	7.617	7.722	7.828	7.936
8	8.045	8.155	8.267	8.380	8.494
9	8.609	8.727	8.845	8.965	9.086
10	9.209	9.333	9.458	9.585	9.714
11	9.844	9.976	10.109	10.244	10.380
12	10.518	10.658	10.799	10.941	11.085
13	11.231	11.379	11.528	11.680	11.833
14	11.987	12.144	12.302	12.462	12.624
15	12.788	12.953	13.121	13.290	13.461
16	13.634	13.809	13.987	14.166	14.347
17	14.530	14.715	14.903	15.092	15.284
18	15.477	15.673	15.871	16.071	16.272
19	16.477	16.685	16.894	17.105	17.319
20	17.535	17.753	17.974	18.197	18.422
21	18.650	18.880	19.113	19.349	19.587
22	19.827	20.070	20.316	20.565	20.815
23	21.068	21.324	21.583	21.845	22.110
24	22.377	22.648	22.922	23.198	23.476
25	23.756	24.039	24.326	24.617	24.912
26	25.209	25.509	25.812	26.117	26.426
27	26.739	27.055	27.374	27.696	28.021
28	28.349	28.680	29.015	29.354	29.697
29	30.043	30.392	30.745	31.102	31.461
30	31.824	32.191	32.561	32.934	33.312
31	33.695	34.082	34.471	34.864	35.261
32	35.663	36.068	36.47	36.891	37.308
33	37.729	38.155	38.564	39.018	39.457
34	39.898	40.344	40.796	41.251	41.710
35	42.175	42.644	43.117	43.595	44.078
36	44.563	45.054	45.549	46.050	46.556
37	47.067	47.582	48.102	48.627	49.157
38	49.692	50.231	50.774	51.323	51.879
39	52.442	53.009	53.580	54.156	54.737
40	55.324	55.91	56.51	57.11	57.72
41	58.34	58.96	59.58	60.22	60.86

Temp. °C	00	02	04	06	08
42	61.50	62.14	62.80	63.46	64.12
43	64.80	65.48	66.16	66.86	67.56
44	68.26	68.97	69.69	70.41	71.14
45	71.88	72.62	73.36	74.12	74.88
46	75.65	76.43	77.21	78.00	78.80
47	79.60	80.41	81.23	82.05	82.87
48	83.71	84.56	85.42	86.28	87.14
49	88.02	88.90	89.79	90.69	91.59
50	92.51	93.5	94.4	95.3	96.3
51	97.20	98.2	99.1	100.1	101.1
52	102.09	103.1	104.1	105.1	106.2
53	107.20	108.2	109.3	110.4	111.4
54	112.51	113.6	114.7	115.8	116.9
55	118.04	119.1	120.3	121.5	122.6
56	123.80	125.0	126.2	127.4	128.6
57	129.82	131.0	132.3	133.5	134.7
58	136.08	137.3	138.5	139.9	141.2
59	142.60	143.9	145.2	146.6	148.0
60	149.38	150.7	152.1	153.5	155.0
61	156.43	157.8	159.3	160.8	162.3
62	163.77	165.2	166.8	168.3	169.8
63	171.38	172.9	174.5	176.1	177.7
64	179.31	180.9	182.5	184.2	185.8
65	187.54	189.2	190.9	192.6	194.3
66	196.09	197.8	199.5	201.3	203.1
67	204.96	206.8	208.6	210.5	212.3
68	214.17	216.0	218.0	219.9	221.8
69	223.78	225.7	227.7	229.7	231.7
70	233.7	235.7	237.7	239.7	241.8
71	243.9	246.0	248.2	250.3	252.7
72	254.6	256.8	259.0	261.2	263.4
73	265.7	268.0	270.2	272.6	274.8
74	277.2	279.4	281.8	284.2	286.6
75	289.1	291.5	294.0	296.4	298.8
76	301.4	303.8	306.4	308.9	311.4
77	314.1	316.6	319.2	322.0	324.6
78	327.3	330.0	332.8	335.6	338.2
79	341.0	343.8	346.6	349.4	352.2
80	355.1	358.0	361.0	363.8	366.8
81	369.7	372.6	375.6	378.8	381.8
82	384.9	388.0	391.2	394.4	397.4
83	400.6	403.8	407.0	410.2	413.6
84	416.8	420.2	423.6	426.8	430.2
85	433.6	437.0	440.4	444.0	447.5
86	450.9	454.4	458.0	461.6	465.2
87	468.7	472.4	476.0	479.8	483.4
88	487.1	491.0	494.7	498.5	502.2
89	506.1	510.0	513.9	517.8	521.8
90	525.76	529.77	533.80	537.86	541.95
91	546.05	550.18	554.35	558.53	562.75
92	566.99	571.26	575.55	579.87	584.22
93	588.60	593.00	597.43	601.89	606.38
94	610.90	615.44	620.01	624.61	629.24
95	633.90	638.59	643.30	648.05	652.82
96	657.62	662.45	667.31	672.20	677.12
97	682.07	687.04	692.05	697.10	702.17
98	707.27	712.40	717.56	722.75	727.98
99	733.24	738.53	743.85	749.20	754.58
100	760.00	765.45	770.93	776.55	782.00
101	787.57	793.18	798.82	804.50	810.21

[a] Handbook of Chemistry and Physics, 45th edition, Chemical Rubber Publishing Company, 1965.

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(Please read Instructions on the reverse before completing)

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16. ABSTRACT

This manual is used in conjunction with Course #435, "Atmospheric Sampling", as designed and presented by the EPA Air Pollution Training Institute (APTI). The manual supplements the course lecture material, presenting detailed discussions in an introductory manner on the following topics:

Basic Gas Properties and Mathematical Manipulations
Air Measuring Instruments
Particulate Sampling
Gaseous Sampling
Generation of Controlled Test Atmospheres
Standard Methods for Criteria Pollutants
Continuous Air Monitoring Instruments
Design of Surveillance Networks
Atmospheric Sampling Statistical Techniques

This Student Manual is designed to be used in conjunction with the Instructor's Guide (EPA 450/2-80-006) and the Laboratory Manual (EPA 450/2-80-005) for APTI Course 435.

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